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Detailed monitoring methods

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ATMOSPHERIC MONITORING

FOR TRANSPORTATION EMERGENCIES

VOLUME III

DETAILED MONITORING METHODS

A Report Prepared for the
Ontario Ministry of the Environment

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METHOD 1a

(ACETIC ACID)

Method Ref:	1a (NIOSH S 169)
Range:	12.5 to 50 mg/m^3
Precision:	$(\overline{CV}_T)$ 0.058
Procedure:	Adsorption on charcoal, desorption with formic acid, GC.

1. APPARATUS

1.1 Personal Sampling Pump

1.2 Charcoal Tubes: Glass tube with both ends flame sealed. 7 cm long with a 6 mm O.D. and a 4 mm I.D., containing two sections of 20.40 mesh activated charcoal separated by a 2 mm portion of urethane foam. The adsorbing section contains 100 mg of charcoal, the backup section 50 mg. A 3 mm portion of urethane foam is placed between the outlet end of the tube and the backup section. A plug of silylated glass wool is placed in front of the adsorbing section.

1.3 Gas chromatograph equipped with a flame ionization detector.

1.4 Column (1 m long x 4 mm I.D. glass) packed with 60/80 mesh Carbo pack B/3% Carbowax 20M/0.5% H_3PO_4.

1.5 An electronic integrator or some other suitable method of determining peak areas.

1.6 Sample Containers: Two-millilitre glass sample containers with glass stoppers or Teflon caps.

1.7 Microfilter Syringes: 10 microlitre and other convenient sizes for preparing standards.

1.8 Pipets: Delivery type, 1.0 ml and other convenient sizes.

1.9 Volumetric Flasks: 10 ml and other convenient sizes for preparing standard solutions.

1.10 Stopwatch.

1.11 Manometre.

2. REAGENTS

2.1 Formic Acid, 88%.

2.2 Glacial acetic acid, reagent grade.

2.3 Nitrogen, purified.

2.4 Hydrogen, prepurified.

2.5 Air, filtered, compressed.

3. PROCEDURE

3.1 Cleaning of Equipment. All glassware used for the laboratory analysis should be detergent washed, throughly rinsed with tap water and distilled water and dried.

3.2 Calibration of Sampling Pumps. Each personal sampling pump must be calibrated with a representative charcoal tube in the line to minimize errors associated with uncertainties in the volume sampled.

3.3 Collection of Samples

3.3.1 Immediately before sampling, break the ends of the charcoal tube to provide an opening at least one-half the internal diameter of the tube. All tubes must be from the same manufacturer's lot.

3.3.2 The smaller section of charcoal is used as a backup and should be positioned nearer the sampling pump.

3.3.3 The charcoal tube should be placed in a vertical direction during sampling to minimize channeling through the charcoal.

3.3.4 Air being sampled should not be passed through any hose or tubing before entering the charcoal tube.

3.3.5 A sample size of 168 litres is recommended. Sample at a flow rate of 1.0 litre per minute or less. Record the sampling time, flow rate, and type of sampling pump used.

3.3.6 The temperature, pressure, and relative humidity of the atmosphere being sampled should be recorded. If pressure reading is not available, record the elevation.

3.3.7 The charcoal tube should be capped with plastic caps immediately after sampling. Under no circumstances should rubber caps be used.

3.3.8 With each batch of ten samples, submit one tube from the same lot of tubes used for sample collection. This tube must be subjected to exactly the same handling as the samples except that no air is drawn through it. This tube should be labelled as the blank.

3.4 Analysis of Samples

3.4.1 Preparation of Samples. In preparation for analysis, each charcoal tube is scored with a file in front of the first section of charcoal and broken open. The glass wool is removed and discarded. The charcoal in the first (larger) section is transferred to a 2 ml stoppered sample container. The separating section of foam is removed and discarded; the second section is transfered to another sample container vial. These two sections are analyzed separately.

3.4.2 Desorption of Samples. Prior to analysis, 1.0 ml of formic acid is pipetted into each sample container. Desorption should be done by 60 minutes.

3.4.3 GC conditions. The typical operating conditions for the gas chromatograph are:

60 ml/min (60 psi) nitrogen carrier gas flow
50 ml/min (24 psi) hydrogen gas flow to detector
500 ml/min (50 psi) air flow to detector
230°C injector temperature
203°C detector manifold temperature
column temperature, program from 130-180°C as described below.

3.4.4 Injection. Inject 5 µl of sample into GC.

4. Calibration and Standards

4.1 Prepare a stock standard solution containing 42 mg/ml acetic acid in formic acid.

4.2 From the above stock solution, appropriate aliquots are withdrawn and dilutions are made in formic acid. Prepare at least 5 working standards to cover the range of 0.42-12.6 mg/1.0 ml. This range is based on a 168-litre sample.

4.3 Prepare a standard calibration curve by plotting concentration of acetic acid in mg/1.0 ml versus peak area.

5. Calculations

5.1 Read the weight, in mg, corresponding to each peak area from the standard curve. No volume corrections are needed if the standard curve is based on mg/1.0 ml formic acid and the volume of sample injected is identical to the volume of the standards injected.

5.2 Corrections for the blank must be made for each sample.

mg = mg sample - mg blank

where:

mg sample = mg found in front section of sample tube

mg blank = mg found in front section of blank tube

A similar procedure is followed for the backup sections.

5.3 Add the weights found in the front and backup sections to determine the total weight of the sample.

5.4 For personal sampling pumps with rotameters only, the following correction should be made.

$$\text{Corrected Volume} = f \times t \times \frac{P_1}{P_2} \times \frac{T_2}{T_1}$$

Where:

f = flow rate sampled

t = sampling time

P_1 = pressure during calibration of sampling pump (mm Hg)

P_2 = pressure of air sampled (mm Hg)

T_1 = temperature during calibration of sampling pump (^{o}K)

T_2 = temperature of air sampled (^{o}K)

5.5 The concentration of acetic acid in the air sampled can be expressed in mg/m^3

$$mg/m^3 = \frac{\text{mg acetic acid x 100 (litres/m}^3\text{)}}{\text{Corrected air volume sampled (litres)}}$$

6. REFERENCES

1. White, L.D., et al., " A Convenient Optimized Method for the Analysis of Selected Solvent Vapors in the Industrial Atmosphere," Amer. Ind. Hyg. Assoc. J., 31, 225, (1970).

2. Documentation of NIOSH Validation Test, NIOSH Contract CDC-99-74-45.

3. Backup Data Report for Acetic Acid, prepared under NIOSH Contract No. 210-76-0123.

METHOD 1b

(ACETIC ACID)

Method Ref:	1b (Suggested method only, proven sampling method not available) ACETIC ACID
Range:	Unknown
Precision:	Unknown
Procedure:	Collection on impregnated Na_2CO_3 W41 filter, extraction with water, I.C.

1. APPARATUS

1.1 Dionex Ion Chromatograph, Model 10 or equivalent.

1.2 Calibrated personal sampling pump.

2. REAGENTS

2.1 Sodium carbonate

2.2 Sodium acetate

2.3 Associated laboratory glassware.

3. PROCEDURE

3.1 Before sampling, 47 mm W41 filter discs are impregnated with 10% sodium carbonate solution.

3.2 Assemble the discs into filter packs and sample with a flow rate of 200 cc/min for 8 hrs.

4. ANALYSIS

4.1 Remove the W41 filter paper to a tube containing 25 mls DIH_2O and shake for 1 hr.

4.2 Inject the supernatant through a 0.45 µ membrane filter into the I.C.

4.3 Typical I.C. conditions are the following.

Eluent: 0.00015 M $NaHCO_3$
Flow Rate: 138 ml/hr
Separator column: 3 x 500 mm Anion Separator
Injection Volume: 100 µl
Metre Full Scale Setting: 3 µMHO/cm

5. REFERENCE

Dionex Corporation: Ion Chromatograph Systems, 1228 Titan Way, Sunnyvale, CA 94086.

METHOD 2

(ACETIC ANHYDRIDE)

Method Ref:	2(NIOSH S170)
Range:	9.35 to 37.4 mg/m^3
Precision:	(CV_T) 0.060
Procedure:	Bubbler Collection, colorimetric

1. APPARATUS

1.1 Sampling Equipment. The sampling equipment for the hauler collection method consists of the following components:

1.1.1 A glass standard midget bubbler with stem which has a fritted glass end and containing the absorbing solution (Section 2.4). The fritted end should have a porosity approximately equal to that of Corning EC (170-220 u maximum pore diameter).

1.1.2 A pump suitable for delivering at least 1 litre per minute for 100 minutes. The sampling pump is protected from splash-over or water condensation by a 5 cm (6mm I.D. and 8mm O.D.) glass tube loosely packed with a plug of glass wool and inserted between the exit arm of the impinger and the pump.

1.1.3 An intergrated volume meter such as a dry gas meter or wet test meter.

1.1.4 Thermometer.

1.1.5 Manometer.

1.1.6 Stopwatch.

1.2 A specrophotometer capable of measuring the developed colour at 540 nm.

1.3 Matched glass cells or cuvettes, 1 cm path length.

1.4 Assorted laboratory glassware - pipets, volumetric flasks, and graduated cylinders of appropriate capacities.

2. REAGENTS

All reagents must be ACS reagent grade or better.

2.1 Distilled water.

2.2 Hydroxylamine hydrochloride solution. Prepare this solution by dissolving 200 g in distilled water in a 1 litre volumetric flask. Dilute to mark with distilled water and transfer the solution to a light protected container. Store the solution in a refrigerator and reject any solution when it is two weeks old.

2.3 Sodium hydroxide solution, Prepare this solution by dissolving 200 g. in distilled water in a 1 litre volumetric flask. Cool the solution to room temperature and dilute to volume.

2.4 Absorbing solution. Mix equal volumes of the hydroxylamine hydrochloride and sodium hydroxide solution. This mixture is stable for only two hours and should be prepared fresh just prior to use.

2.5 Ferric chloride solution. Pipet 10 ml of acetic anhydride into a 100 ml volumetric flask and make a volume with acetone. The solution must be prepared within two hours of use.

3. PROCEDURE

3.1 Cleaning of equipment. No specialized cleaning of glassware is required. However, since known interferences occur with esters and aldehydes, cleaning techniques should insure the absence of all organic materials.

3.2 Calibration of personal sampling pump. The pump should be calibrated using an integrating volume meter or other means.

3.3 Collection of Samples.

3.3.1 Pour 10 ml of the absorbing solution (Section 2.4) into each bubbler.

3.3.2 Connect the bubbler with a 5 cm glass adsorption tube (6 mm I.D. and 8 mm O.D.) containing the glass wool plug, then to the personal sampling pump using short pieces of flexible tubing. The air being sampled should not pass through any tubing before entering the bubbler.

3.3.3 Turn on pump to begin sample collection. Care should be taken to measure the flow rate, the time and/or volume as accurately as possible. Record atmospheric pressure and temperature. If pressure reading is not available. Record the elevation. The sample should be taken at a flow rate of 1 litre per minute. A sample size of 100 litres is recommended.

3.3.4 After sampling, the bubbler stem can be removed and cleaned. Tap the stem gently against the inside wall of the bubbler bottle to recover as much of the sampling solution as possible. Wash the stem with 1-2 ml of the absorbing solution and add the wash to the bubbler. Seal the bubbler with a hard, non-reactive stopper (preferably Teflon or glass). Do not seal with rubber. The stoppers on the bubblers should be tightly sealed to prevent leakage during shipping.

3.3.5 A "blank" bubbler should be handled as the other samples (fill, seal, and transport) except that no air is sampled through this bubbler.

3.4 Analysis of Samples

3.4.1 The sample in each bubbler is analyzed separately.

3.4.2 Transfer the solution to a 50-ml volumetric flask.

3.4.3 Rinse the bubbler twice with 1 ml of distilled water and add the rinses to the volumetric flask.

3.4.4 Pipet 5 ml of the ferric chloride solution into the volumetric flask.

3.4.5 Dilute to the mark with a solution containing equal volumes of sodium hydroxide solution, hydroxylamine hydrochloride solution and ferric chloride solution. This solution should be made in an ice bath. The purple complex is formed rapidly.

3.4.6 Read the absorbance at 540 nm in the spectrophotometer against a blank prepared from the alkaline hydroxylamine solution and ferric chloride in the same fashion as the samples.

4. CALIBRATION AND STANDARDS

4.1 Preparation of the calibration curve.

4.1.1 Pipet 10 ml. of the absorbing solution into six 50 ml volumetric flasks.

4.1.2 Carefully transfer 0 (blank), 10, 20, 40, 80, and 100 micro-litres of the standard solution into the flasks (Section 2.6).

4.1.3 Add to this mixture 5 ml of ferric chloride solution (Section 2.5) using a 5 ml pipet.

4.1.4 Continued as described in Section 3.4.5.

4.1.5 Adjust the baseline of the spectrophotometer to zero with distilled water in both cells.

4.1.6 Measure the absorbance of the blank and standards at 540 nm.

4.1.7 Construct a calibration curve by plotting absorbance against equivalent milligrams of acetic anhydride.

5. CALCULATIONS

5.1 Subtract the absorbance of the blank from the absorbance of each sample.

5.2 Determine from the calibration curve the mg of acetic anhydride present in each sample.

5.3 The concentration of acetic anhydride can be expressed in a similar way as Method 1a.

6. REFERENCES

1. Diggle, W.M. and Gage, J.C., "The Determination of Ketene and Acetic Anhydride in the Atmosphere," Analyst, 78, 473 (1953).

2. Documentation of NIOSH Validation Test, NIOSH Contract No. CDC-99-74-45.

METHOD 3

(ACETONITRILE)

Method Ref:	3(NIOSH S165)
Range:	31.4 to 140.2 mg/m^3
Precision:	$(\overline{CV}_T)$ 0.072
Procedure:	Adsorption on charcoal, desorption with benzene, GC.

1. APPARATUS

1.1 A calibrated personal sampling pump.

1.2 Charcoal tubes: Glass tube with both ends flame sealed, 9 cm long with a 8 mm O.D. and 6 mm I.D., containing 2 sections of 20/40 mesh activated charcoal separated by a 2 mm portion of urethane foam. The adsorbing section contains 400 mg of charcoal, the backup section 200 mg.

1.3 Gas chromatograph equipped with a flame ionization detector.

1.4 Column (4-ft x 1/4 in stainless steel) packed with 50/80 mesh Porapak, Type Q.

1.5 An electronic integrator or some other suitable method for measuring peak areas.

1.6 Volumetric flasks: 10 ml or convenient sizes for making standard solutions and for desorbing the samples.

1.7 Microlitre syringes: 10-microlitre for injection of samples into the gas chromatograph.

1.8 Pipets: 5 ml delivery pipets.

2. REAGENTS

2.1 Chromatographic quality benzene.

2.2 Acetonitrile, reagent grade.

2.3 Purified nitrogen.

2.4 Prepurified Hydrogen.

2.5 Filtered compressed air.

METHOD 3

(ACETONITRILE)

(cont'd)

3. PROCEDURE

3.1 Cleaning of Equipment: Follow Method 1a.

3.2 Calibration of Personal Pumps: Follow Method 1a.

3.3 Collection of Samples

3.3.1 Follow procedure outlined in Method 1a.

3.3.2 A sample size of 10 litres is recommended. Sample at a flow of 0.20 litres per minute or less.

3.4 Analysis of Samples

3.4.1 Preparation of Samples. Similar to Method 1a.

3.4.2 Desorption of Samples. Prior to analysis, 5 ml of benzene is pipetted into each sample container. Desorption should be done for 30 minutes.

3.4.3 GC conditions. The typical operating conditions for the gas chromatograph are:

1. 50 ml/min (60 psig) nitrogen carrier gas flow.
2. 65 ml/min 924 psig) hydrogen gas flow to detector.
3. 500 ml/min (50 psig) air flow to detector.
4. 270°C injector temperature.
5. 285°C manifold temperature (detector).
6. 180°C column temperature.

3.4.4 Injection. Inject 5 µl of sample into GC.

4. CALCULATIONS

4.1 Similar to that presented in Method 1a. Read the weight, in mg, corresponding to each peak area from the standard curve. No volume corrections are needed, if the standard curve is based on mg/5.0 ml benzene and the volume of sample injected is identical to the volume of the standards injected.

5. REFERENCES

1. White, L.D. et al., "A Convenient Optimized Method for the Analysis of Selected Solvent Vapors in the Industrial Atmosphere", Amer. Ind. Hyg. Assoc. J., 31: 225 (1970).

2. Documentation of NIOSH Validification Tests, NIOSH Contract No. CDC-99-74-45.

3. Final Report, NIOSH Contract HSM-99-71-31, "Personal Sampler Pump for Charcoal Tubes", 15 September 1972.

METHOD 4

(ACRYLONITRILE)

Method Ref:	4(P & CAM 202)
Range:	40 to 1100 mg/m^3 in a 20 litre sample
Precision:	($\overline{CV}_T$) 0.10 at 150 to 200 mg/m^3 in a 10 litre sample
Procedure:	Adsorption on Carbosieve B, desorption with methanol, gas chromatographic determination.

1. APPARATUS

1.1 A Properly Calibrated Personal Sampling Pump. The pump should be calibrated with a representative sorbent tube in the sampling line. A dry or wet test meter or a glass rotameter that will determine the appropriate flow rate (<1 1/min) to within ±5% may be used for the calibration.

1.2 Sorbent Tubes. The glass tubes have both ends flame sealed. Each is 8 cm long with a 7 mm O.D. and a 5 mm I.D. They contain two sections of 45/60 mesh Carbosieve B, separated by a 2 mm portion of glass wool. Carbosieve B is a pyrolyzed Saran manufactured and distributed by Supelco, Inc., Bellafonte, Pennsylvania. The sorbing section contains 150 mg of sorbent, the backup section 50 mg. A 3 mm plug of glass wool is placed between the outlet end of the tube and the backup section. A 3 mm plug of glass wool is also placed in front of the sorbing section.

1.3 Gas chromatograph equipped with a flame ionization detector.

1.4 A stainless steel column (9 ft. x 0.125 I.D.) with 50/80 mesh Porapak N as the stationary phase.

1.5 A recorder and an appropriate means of determining peak area.

1.6 Vials with plastic caps (2 dram).

1.7 Gas chromatographic liquid syringe (10 µl).

1.8 Volumetric pipettes of appropriate sizes.

2. REAGENTS

2.1 Methanol, reagent grade.

2.2 Purified nitrogen.

2.3 Prepurified hydrogen.

2.4 Filtered compressed air.

2.5 Acrylonitrile, >99% pure.

2.6 Acrylonitirle, Standard Solution (10 mg/ml). Dilute 1.000 g of acrylonitrile to 100 ml with methanol. This standard is stable for at least 2 weeks at ambient temperatures.

3. PROCEDURE

3.1 Cleaning of Equipment. Follow procedure outlined in Method 1a.

3.2 Collection of Samples

3.2.1 Follow procedure outlined in Method 1a.

3.2.2 Sample should be taken at a flow rate of 1 l/min or less. The minimum and maximum sample volumes that should be collected for acrylonitrile are 10 litres and 95 litres, respectively.

3.2 Analysis of Samples

3.3.1 Preparation of samples: Similar to that outlined in Method 1a.

3.3.2 Desorption of samples: Prior to analysis, 2 ml of methanol is added to the vial containing the first sorbent section, and 1 ml to the vial containing the backup layer. Desorption is complete after 3 to 4 min if the sample is agitated frequently. No loss of sample or desorbing solvent has been noted if the vial is stoppered with a plastic cap during the desorption process.

3.3.3 Gas Chromatrographic Conditions. Typical operating conditions for the gas chromatograph are:

1. Nitrogen carrier gas flow, 40 ml/min.
2. Hydrogen gas flow to detector, 40 ml/min.
3. Air flow to detector 300 ml/min.
4. Injection temperature, 200°C.
5. Column temperature 170°C.

6. Detector temperature, 170°C. (In general, the detector temperature should be higher than the column temperature. However, the gas chromatograph used in the development of this method required a common temperature for both.)

3.3.4 Injection: Inject 2 µl of sample.

4. CALCULATIONS

4.1 Similar to that outlined in Method 1a.

4.2 Read the weight in mg, corresponding to each peak are from the standard curve. No volume corrections are needed, if the standard curve is based on mg/2.0 ml and the volume of sample injected is identical to the volume of the standards injected.

5. REFERENCES

1. Barrett, W.J., Dillon, H.K., and James, R.H., "Sampling and Analysis of Four Organic Compounds Using Solid Sorbents," Southern Research Institute, Birmingham, Alabama, Final Report for Contract No. HSM 99-73-63 to the National Institute for Occupational Safety and Health, Division of Laboratories and Criteria Development, Physical and Chemical Analysis Branch, Cincinnati, Ohio 1974, pp. 53-77, 105-114.

2. White, L.D., Taylor, D.G., Mauer, P.A., and Kupel, R.E., "A Convenient Optimized Method for the Analysis of Selcted Solvent Vapors in the Industrial Atmosphere," Amer. Ind. Hyg. Assoc. J., 31, 225 (1970).

METHOD 5

(METALS)

Method Ref: 5 (P & CAM 173)
Range: Varies with analyte (Table 2)
Precision: 3% RSD (Analytical)

1. APPARATUS

1.1 Sampling Equipment. The sampling unit for the collection of personal air samples has the following components:

1.1.1 The filter unit, consisting of the filter media and appropriate casette filter holder, either a 2 or 3 piece filter casette.

1.1.2 A personal sampling pump of sufficient capacity to maintain a face velocity of 2.6 cm/sec (1-2 L/min using a 37 mm filter).

1.1.3 Thermometer.

1.1.4 Manometer.

1.1.5 Stopwatch.

1.1.6 Various clips, tubing, spring connectors, and belt for connecting sampling apparatus to worker being sampled.

1.2 Cellulose ester membrane filter, 0.8 µm pore size, 37 mm (Millipore Type AA or equivalent).

1.3 Glassware, borosilicate. Before use, all glassware must be cleaned in 1:1 diluted nitric acid and rinsed several times with distilled water.

1.3.1 125 ml Phillips or Griffin beakers with watch glass covers.

1.3.2 15 ml graduated centrifuge tubes.

1.3.3 10 ml volumetric flasks.

1.3.4 100 ml volumetric flasks.

1.3.5 1 litre volumetric flasks.

1.3.6 125 ml polyethylene bottles.

1.4 Hot plates (suitable for operation at 140°C).

1.5 Equipment for Analysis

1.5.1 Atomic absorption spectrophotometer, with burner heads for air-acetylene and nitrous oxide-acetylene flames.

1.5.2 Hollow cathode or electrodeless discharge lamps, for each metal and a continuum lamp (D_2 or H_2).

1.5.3 Two stage regulators, for air, acetylene, and nitrous oxide.

1.5.4 Heating tape and rheostat, for nitrous oxide regulator (second regulator stage and connecting hose to the instrument should be heated to approximately 60°C to prevent freeze-up).

1.6 Supplies

1.6.1 Acetylene gas (cylinder), of a grade specified by the manufacturer of the instrument employed. (Replace cylinder when pressure decreases below 100 psi.)

1.6.2 Nitrous oxide gas (cylinder).

1.6.3 Air supply, with a minimum pressure of 40 psi, filtered to remove oil and water.

2. REAGENTS

2.1 Purity, ACS analytical reagent grade chemicals or equivalent shall be used in all tests. References to water shall be understood to mean double distilled water or equivalent. Care in selection of reagents and in following the listed precautions is essential if low blank values are to be obtained.

2.2 Concentrated nitric acid (68-71%), redistilled, specific gravity 1.42.

2.3 Standard stock solutions (1000 µg/ml).

2.4 Lanthanum nitrate $La(NO_3)_3\ 6H_2O$.

2.5 Cesium nitrate ($CsNO_3$).

3. PROCEDURE

3.1 Cleaning of Equipment

3.1.1 Before initial use, glassware is cleaned with a saturated solution of sodium dichromate in concentrated sulfuric acid (Note: Do not use for chromium analysis) and then rinsed thoroughly with warm tap water, concentrated nitric acid, tap water, and deionized water, in that order, and then dried.

3.1.2 All glassware is soaked in a mild detergent solution immediately after use to remove any residual grease or chemicals.

3.1.3 For glassware which has previously been subjected to the entire cleaning procedure, it is not necessary to use the chromic acid cleaning solution.

3.2 Collection of Samples

3.2.1 Ambient atmospheric particulate matter and industrial dusts and dumes are sampled with cellulose membrane filters. Sample flow rate is monitored with a calibrated rotameter or the equivalent. The flow rate, ambient temperature, and barometric pressure are recorded at the beginning and the end of the sample collection period.

3.2.2 For personal sampling, 37 mm diameter filters in holders are used. The personal sampling pumps for this application are operated at 1.5 L/min. In general, a 2 hour sample at 1.5 L/min. will provide enough sample to detect the elements sought at air concentrations of 0.2 x TLV.

3.2.3 After sample collection is complete, plug the openings of the casette and submit the sampling unit to the laboratory. Losses of sample due to overloading (>2 mg) of the filter must be avoided.

3.2.4 Filter samples should be sealed in individual plastic filter holders for storage and shipment.

3.3 Preparation of Samples

3.3.1 The samples and blanks (minimum of 1 filter blank for every 10 filter samples) are transferred to clean 125 ml Phillips or Griffin beakers and 0.6 ml HNO_3 is added. Each beaker is covered with a watch glass and heated on a hot plate (140^{o} C) in a fume hood until the sample dissolves and a slightly yellow solution is produced. Approximately 4 hours of heating will be sufficient for most air samples. However, subsequent additions of HNO_3 may be needed to completely ash and destroy high concentrations of organic material and

under these conditions longer ashing times will be needed. Once the ashing is complete as indicated by a clear solution in the beaker, the watch glass is removed and the sample is allowed to evaporate to near dryness (approximately 0.5 ml).

3.3.2 Remove the beaker from the hotplate, cool and add 1 ml HNO_3 and 2-3 ml of distilled H_2O. For lead samples, concentrated HCl is used instead of HNO_3. The solution is quantitatively transferred with distilled water to a 10 ml volumetric flask. 0.2 ml of 50 mg/ml Cs is added to the volumetric flask.

0.2 ml of 50 mg/ml La is added to each volumetric flask. The samples are then diluted to volume with water.

3.3.3 The 10 ml solution may be analyzed directly for any element of very low concentration in the sample. Aliquots of this solution may then be diluted to an appropriate volume for the other elements of interest present at higher concentrations.

3.4 Analysis of Samples

3.4.1 Set analytical wavelength at 309.3 nm for Al.

3.4.2 Standard solutions should match the sample matrix as closely as possible and should be run in duplicate. Working standard solutions, prepared fresh daily, are aspirated into the flame and the absorbance recorded. Prepare a calibration graph as described in Section 4.2.3. (Note: All combustion products from the AA flame must be removed by direct exhaustion through the use of a good separate flame ventilation system.)

3.4.3 Blank filters must be carried through the entire procedure each time samples are analyzed.

3.4.4 Aspirate the appropriately diluted samples directly into the instrument and record the absorbance for comparison with standards. Should the absorbance be above the calibration range, dilute an appropriate aliquot to 10 ml. Aspirate water between each sample. A mid-range standard must be aspirated with sufficient frequency (i.e. once every 5 samples) to assure the accuracy of the sample determinations. to the extent possible, all determinations are to be based on replicate analysis.

4. CALIBRATION AND STANDARDS

4.1 Ionization and chemical interference suppressants.

4.1.1 Lanthanum solution (50 mg/ml). Dissolve 156.32 g of lanthanum nitrate La $(NO_3)_3$ $6H_2O$ in 2% (v/v) HNO_3.

Dilute to volume in a 1 litre volumetric flask with 2% (v/v) HNO_3. When stored in a polyethylene bottle, this solution is stable for at least one year.

4.1.2 Cesium solution (50 mg/ml). Dissolve 73.40 g of cesium nitrate ($CsNO_3$) in distilled water. Dilute to volume in a 1 litre volumetric flask with distilled water. When stored in polyethylene bottle this solution is stable for at least one year.

4.2 Standard metal solutions.

4.2.1 Dilute standards (100 µg metal/ml). Pipet 10 ml of the stock (1000 µg metal/ml; Section 2.3) into a 100 ml volumetric flask, add 10 ml HNO_3 and dilute to volume with distilled water. Prepare these standards fresh weekly.

4.2.2 Working standards. Working standards for each metal of interest are prepared by dilution of the dilute standards (4.2.1) or the stock standards (2.3) such that the final acid concentration is the same for the samples and standards (i.e. 10 % v/v HNO_3 in most cases). Lanthanum or cesium is added to samples and standards, such that the final concentration is 1000 µg La or Cs/ml. Prepare these solutions fresh daily.

4.2.3 The standard solutions are aspirated into the flame and the absorbance (or concentration) recorded). If the instrument used displays transmittance, these values must be converted to absorbance. A calibration curve is prepared by plotting absorbance versus metal concentration. The best fit curve (calculated by linear least square regression analysis) is fitted to the data points. This line or the equation discribing the line is used to obtain the metal concentration in the samples being analyzed.

5. CALCULATIONS

5.1 The uncorrected volume collected by the filter is calculated by averaging the beginning and ending sample flow rates, converting to cubic metre and multiplying by the sample collection time. The formula for this calculation is:

$$V = \frac{(F_B + F_E)t}{2000}$$

Where:

V = sample volume (m^3)

F_B = sample flow rate at beginning of sample collection (lpm)

F_E = sample flow rate at end of sample collection (lpm)

t = sample collection time (minutes)

5.2 After any necessary correction for the blank has been made, metal concentrations are calculated by multiplying the micrograms of metal per ml in the sample aliquot by the aliquot volume and dividing by the fraction which the aliquot represents of the total sample and the volume of air collected by the filter:

$$\mu g \text{ metal}/m^3 = \frac{(C \times V_A) - B}{V \times F}$$

Where:

C = concentration (μg metal/ml) in the aliquot

V_A = volume of aliquot (ml)

B = total μg of metal in the blank

F = fraction of total sample in the aliquot used for measurement (dimensionless)

V = volume of air sampled (m^3)

6. REFERENCES

1. Slavin, W., Atomic Absorption Spectroscopy, Interscience Publishers, New York, 1968.

2. Ramirez-Munoz, J., Atomic Absorption Spectroscopy, Elsevier Publishing Company, New York, 1968.

3. Dean, J.A. and Rains, T.C., Eds., Flame Emission and Atomic Spectrometry: Volume 1, Theory, Marcel Kekker, New York, 1969.

4. Winefordner, J.D., Ed., Spectrochemical Methods of Analysis, John Wiley & Sons, Inc., 1971.

5. Air Sampling Instruments for Evaluation of Atmospheric Contaminants, American Conference of Governmental Industrial Hygienists, 1971.

6. Analytical Methods for Atomic Absorption Spectrophotometry. The Perkin Elmer Corporation, Norwalk, Connecticut, 1976.

7. Belcher, C.B, Dagnall, R.M., and West, T.S., "An Examination of the Atomic Absorption Spectroscopy of Silver", Talanta 11:1257, 1964.

8. Mulford, C.E., "Gallium and Indium Determinations by Atomic Absorption", At Absorpt Newsl 5:28, 1966.

9. Robinson, J.W., Atomic Absorption Spectroscopy, Marcel Dekker, Inc., New York, 1966.

10. Analytical Data for Elements Determined by Atomic Absorption Spectroscopy, Varian Techtron, Walnut Creek, California, 1971.

11. Detection Limites for Model AA-5 Atomic Absorption Spectrophotometer, Varian Techtron, Walnut Creek, California, 1971.

METHOD 6

(AMMONIA AND AMMONIUM HYDROXIDE)

Method Ref:	6
Range:	Unknown
Precision:	Unknown
Procedure:	Collection on oxalic acid coated denuder tubes, extraction in water, IC.

1. APPARATUS

   1.1 Calibrated sampling pump.

   1.2 Denuder tubes and filter packs.

2. REAGENTS

   2.1 Methanol, absolute

   2.2 Oxalic acid

3. PROCEDURE

   3.1 Tubes are coated with a 10% oxalic acid methanolic solution.

   3.2 With the aid of a pipet bulb the oxalic acid solution is drawn up the denuder tube to a height of 35 cm.

   3.3 Ammonia free and dry air is passed through the coated tubes to dry them.

   3.4 Immediately after drying, the tubes are sealed at both ends with parafilm.

   3.5 Prior to sampling, the denuder tubes are assembled into a teflon filter pack which is loaded with an oxalic acid impregnated filter for "carry over" NH_3 capture.

   3.6 The filter pack is connected to a sampling bottle, sequential sampler, flowmeter and recorder. See figure 1 for sampler configuration.

   3.7 A flow rate of 10 l/min and a sampling time of 6 hrs. is recommended.

4. ANALYSIS OF SAMPLES

   4.1 Immediately after sampling, the ends are sealed off with parafilm.

METHOD 6

(AMMONIA AND AMMONIUM HYDROXIDE)

(cont'd)

4.2 Desorption of samples. Prior to analysis, 20 mls of deionized water is pipetted into each sample container. The denuder tubes are extracted by drawing up liquid three times through the tubes.

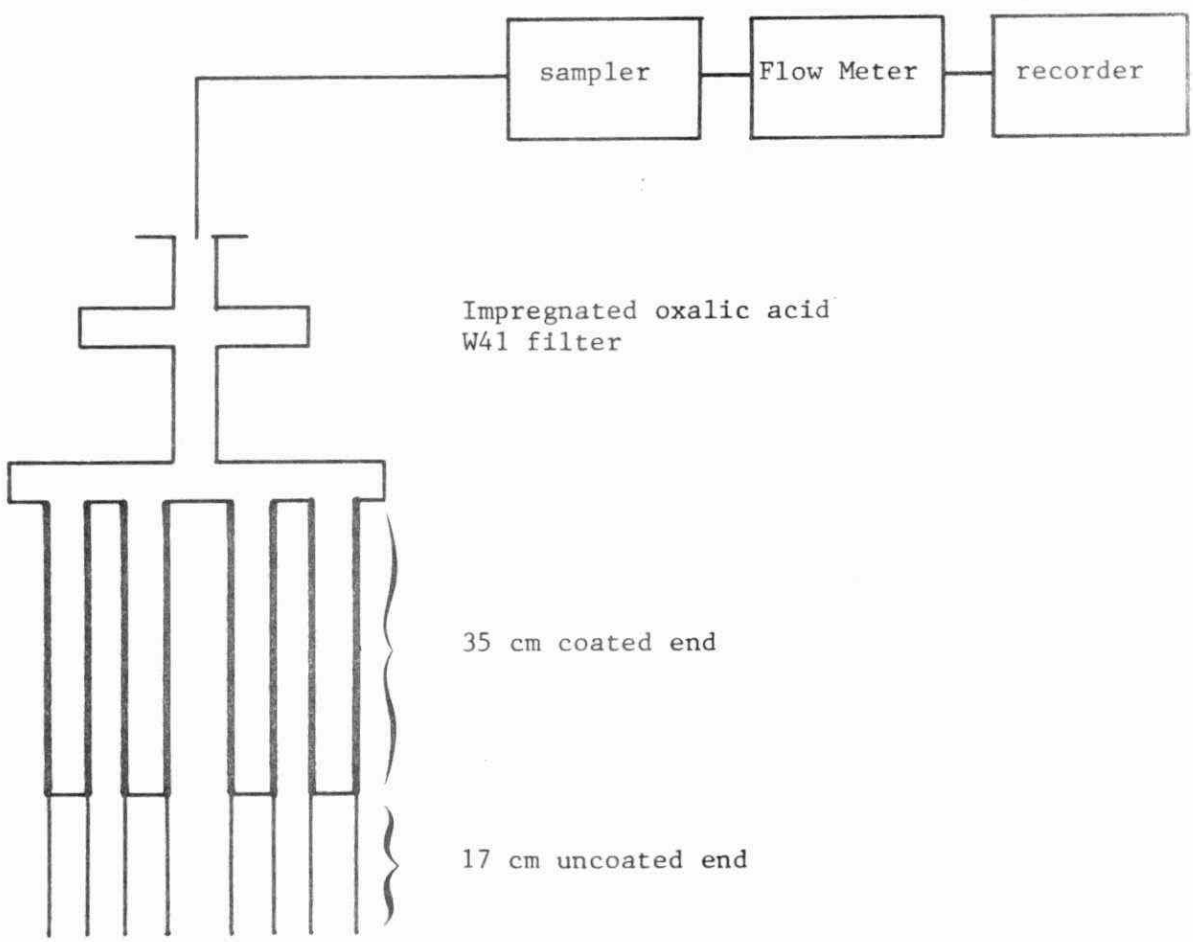
4.3 IC conditions. The typical operating conditions for the ion chromotograph are:

1. Eluent: 0.005 N HNO_3
2. Flow rate: 2.3 ml/min (30%)
3. Pre Column: 3 x 150 mm
4. Cation Separator Column: 6 x 250 mm
5. Cation Suppressor Column: 9 x 250 mm
6. Injection volume: 10 µl
7. Meter full scale setting: µMHO/cm.

5. CALCULATIONS

These are computed in a similar manner as Method 1.

FIGURE 1 - SAMPLE CONFIGURATION



METHOD 7

(ANILINE)

Method Ref:	7 (NIOSH S310) Aniline
Range:	9.54 to 38.2 $\mu g/m^3$
Precision:	$(\overline{CV}_T)$ 0.060
Procedure:	Adsorption on silica gel, desorption with 95% ethanol, GC.

1. APPARATUS

1.1 A calibrated personal sampling pump.

1.2 Silica gel tubes: glass tube with both ends flame sealed, 7 cm long with 6 mm O.D. and a 4 mm I.D., containing 2 sections of 20/40 mesh silica gel separated by a 2 mm portion of urethane foam. The adsorbing section contains approximately 150 mg of silica gel, the backup section, approximately 75 mg.

1.3 Gas chromatograph equipped with a flame ionization detector.

1.4 Column (2 ft x 1/8 in. I.D. stainless steel) packed with Chromosorb 103 (80.100 mesh).

1.5 An electronic integrator or some other suitable method for measuring peak areas.

1.6 Two millilitre sample containers with glass stoppers or Telfon-lined caps. If an automatic sample injector is used, the associated vials may be used.

1.7 Ultrasonic bath.

1.8 Microlitre syringes: 10 microlitre, and other convenient sizes for making standards.

1.9 Pipets: 1.0 ml delivery pipets.

1.10 Volumetric flasks: 10 ml or convenient sizes for making standard solutions.

2. REAGENTS

2.1 Ehtanol, 95%.

2.2 Aniline, reagent grade.

2.3 Benzene, reagent grade.

2.4 n-Hexane, reagent grade.

2.5 Prepurified hydrogen.

2.6 Filtered compressed air.

2.7 Purified nitrogen.

3. PROCEDURE

3.1 Cleaning of Equipment. See Method 1a.

3.2 Calibration of Personal Pumps. See Method 1a.

3.3 Collection of Samples.

3.3.1 See Method 1

A sample size of 20 litres is recommended. Sample at a flow of 0.20 litres per minute or less. The flow rate should be known with an accuracy of at least $\pm$5%.

3.4 Analysis of Samples.

3.4.1 Preparation of Samples: See Method 1a.

3.4.2 Desorption of Samples. Prior to analysis, 1.0 ml of 95% ethanol is pipetted into each sample container. The sample is desorbed for one hour using an ultrasonic bath to aid desorption.

3.4.3 GC Conditions. The typical operating conditions for the gas chromatograph are:

1. 50 ml/min (60 psig) nitrogen carrier gas flow
2. 65 ml/min (24 psig) hydrogen gas flow to detector
3. 500 ml/min (50 psig) air flow to detector
4. 230°C injector temperature
5. 245°C manifold temperature (detector)
6. 165°C column temperature

3.4.4 Injection. Inject a 5 µl aliquot.

4. CALCULATIONS

These are computed in a similar manner as Method 1a.

No volume corrections are needed, if the standard curve is based on mg/1.0 ml 95% ethanol and the volume of sample injected is identical to the volume of the standards injected.

5. REFERENCES

1. Campbell, E.E., Wood G.O., and Anderson, R.G., Los Alamos Scientific Laboratory Progress Reports LA-5104-PR, LA-5164-PR, LA-5308-PR, LA-5389-PR, LA-5484-PR, and LA-5634-PR, Los Alamos, N.M., November 1972, January 1973, August 1973, December 1973, and June 1974.

2. Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.

3. Final Report, NIOSH Contract HSM-99-71-31, "Personal Sampler Pump for Charcoal Tubes," 15 September 1972.

METHOD 8

(BENZENE)

Method Ref:	8 (NIOSH S311)
Range:	13 to 51.8 ppm
Precision:	($\overline{CV}_T$) 0.059
Procedure:	Adsorption on charcoal, desorption with carbon disulfide, GC

1. APPARATUS

1.1 A calibrated personal sampling pump.

1.2 Charcoal tubes: See Method 1a.

1.3 Gas chromatograph equipped with a flame ionization detector.

1.4 Column (3 ft. x 1.8 in. O.D. stainless steel) packed with 50/80 mesh Porapak, Type Q.

1.5 An electronic integrator or some other suitable method for measuring peak areas.

1.6 Two millilitre sample containers with glass stoppers or Teflon-lined caps. If an automatic sample injector is used, the associated vials may be used.

1.7 Microlitre syringes: 10 microlitre, and other convenient sizes for making standards.

1.8 Pipets: 1.0 ml delivery pipets.

1.9 Volumetric flasks: 10 ml or convenient sizes for making standard solutions.

2. REAGENTS

2.1 Chromatographic quality carbon disulfide.

2.2 Benzene, reagent grade.

2.3 Hexane, reagent grade.

2.4 Purified nitrogen.

2.5 Prepurified hydrogen.

2.6 Filtered compressed air.

METHOD 8

(BENZENE)

(cont'd)

3. PROCEDURE

3.1 Cleaning of Equipment. See Method 1a.

3.2 Calibration of Personal Pumps. See Method 1a.

3.3 Collection of Samples

3.3.1 See Method 1. At the ceiling concentration, a sample size of 2 litres is recommended. Sample for 10 minutes at a flow rate of 0.20 litres per minute.

3.3.2 At the 8 hour time weighted average concentration, a sample size of 12 litres is recommended. Sample at a flow rate of 0.20 litres per minute.

3.4 Analysis of Samples

3.4.1 Preparation of Samples. See Method 1a.

3.4.2 Desorption of Samples. Prior to analysis, 1.0 ml of carbon disulfide is pipetted into each sample container.

3.4.3 GC Conditions. The typical operating conditions for the gas chromatograph are:

1. 50 ml/min (60 psig) nitrogen carrier gas flow
2. 65 ml/min (24 psig) hydrogen gas flow to detector
3. 500 ml/min (50 psig) air flow to detector
4. 200°C injector temperature
5. 265°C minifold temperature (detector)
6. 115°C column temperature.

3.4.4 Injection. A 5 µl aliquot is injected.

4. CALCULATIONS

4.1 Read the weight, in mg, corresponding to each peak area from the standard curve. No volume corrections are needed, if the standard curve is based on mg/1.0 ml carbon disulfide and the volume of sample injected is identical to the volume of the standards injected. See Method 1a for computation of results.

5. REFERENCES

1. White, L.D., et al., "A Convenient Optimized Method for the Analysis of Selected Solvent Vapors in the Industrial Atmosphere," Amer. Ind. Hyg. Assoc. J., 31: 225 (1970).

2. Documentation of NIOSH Validation Tests, NIOSH Contract CDC-99-74-45.

3. Final Report, NIOSH Contract HSM-99-71-31, "Personal Sampler Pump for Charcoal Tubes," 15 September 1972.

METHOD 9a

(BROMINE)

Method Ref;	9a
Range:	Nominal detection limit is 2 ng/ml of Br
Precision:	Standard deviation of 2.1% on an arbitrary 0 to 100%
Procedure:	High volume air filter collection, dissolution in flourescein, glacial acetic acid and 30% H_2O_2, flourometric determination.

1. APPARATUS

1.1 Sampling equipment: High volume samplers with collection on glass fiber filters.

1.2 Fluorescence Spectrometer equipped with xenon lamp source, (continuous spectrum).

1.3 1 cm quartz cells.

2. REAGENTS

All reagents used must be AR - grade or better.

2.1 Water, distilled or deionized.

2.2 Glacial acetic acid.

2.3 30% hydrogen peroxide.

2.4 1.1×10^{-6}M fluorescein made up in glacial acetic acid.

2.5 Sodium bromide.

3. PROCEDURE

3.1 Analysis of Samples

3.1.1 After sampling, cut a small section of glass fiber filter and wash with refluxing water to dissolve any collected Br^-.

3.1.2 Add 0.5 ml Br sample to 9.0 ml solution of 1.1×10^{-6}M fluorescein and 0.5 ml of 30% H_2O_2.

3.1.3 Allow 45 minutes after sample addition for complete reaction.

3.1.4 Measure the fluorescence of sample at 440 nm excitation and 460 nm emission.

METHOD 9a

(BROMINE)

(cont'd)

3.1.5 Measure the blank, which is made from the fluorescein glacial HOAC solution, H_2O_2 and water at 440 nm emission and 470 nm excitation.

3.2 Calibration and Standards

3.2.1 Prepare standards from NaBr and treat identically to the samples.

3.2.2 The fluorescence is quenched by the Br, and the quenching amount can be related to the Br concentration through sample standards.

4. CALCULATIONS

4.1 Read the Br value from the analytical curve.

4.2 Correction for the blank must be made for each sample.

µg = µg sample - µg blank

4.3 The concentration of the bromine in the air sampled can be expressed in ng/m^3.

$$ng/m^3 = \frac{\mu g \text{ of bromine found}}{\text{volume of air sampled (litres)}}$$

5. REFERENCE

Axelrod, Herman D. Bonelli, Joseph E., and Lodge, James P. Jr., Env. Science and Technology, 5 420 (1971).

METHOD 9b

(BROMINE)

Method Ref:	9b
Range:	Unknown
Precision:	Unknown
Procedure:	Collection on activated charcoal, neutron activation analysis.

1. APPARATUS

1.1 Vacuum Pump. The gas collector of an electrostatic precipitator, for removal of particulate matter followed by a 2 gram bed of precleaned activated charcoal.

2. REAGENTS

2.1 Activated charcoal

2.2 1 M sodium hydroxide

2.3 5% sodium hypochlorite

2.4 0.5 M Sodium thiosulfate.

3. PROCEDURE

3.1 Preparation of Samples

3.1.1 The charcoal is precleaned by heating to 750°C for two weeks in a vacuum of approximately 10 cm Hg.

3.2 Analysis of Samples

3.2.1 Samples are analyzed by neutron activation analysis (reference 1).

3.2.2 After 20 minutes irradiation with neutrons, the sample is agitated with a hot 1 M NaOH solution containing a few drops of a 5% sodium hypochlorite solution and bromate carrier.

3.2.3 A few drops of 0.5 M $Na_2S_2O_3$ is added to the solution.

3.2.4 The slurry is filtered and the bromine is chemically separated from the filtrate (reference 2, 3) before beta counting.

METHOD 9b

(BROMINE)

(cont'd)

4. REFERENCES

1. Moyers, J.L., Ph. D. Thesis, University of Hawaii, Honolulu, Hawaii, 1970.

2. Duce, R.A., Winchester, J.W. and VanNahl, T.W., Geophys, J. Res. 70 1775 (1965).

METHOD 9c

(BROMINE)

Method Ref;	9c
Range:	Nominal detection limit 0.5 ppm
Precision:	RSD 2.8%
Procedure:	Spectrophotometric monitoring, flow injection analysis.

1. APPARATUS

Spectrophotometric unit equipped with a light source (osram lamp), monochromator, injection, rotary valve and reaction cell chamber, and a detector.

2. REAGENTS

2.1 Arsenic (III) bromide

2.2 X - napthoflavone

2.3 Ethanol, 95% reagent grade

2.4 Bromine gas (prepared from reagent grade bromine).

3. SUPPLIES

Purified compressed air.

4. PROCEDURE

4.1 Analysis of Samples

4.1.1 Spot 0.10 ml of a solution containing 0.05 M arsenic (III) bromide napthoflavone and 1.8×10^{-2} M x-napthoflavone in 95% ethanol on a 1.5 cm x 1.5 cm square of filter paper.

4.1.2 Dry filter paper on a hot plate ($40^{\circ}C$) for 2 minutes.

4.1.3 Place filter paper on the cell drawer of the spectrophotometer unit and insert into the cell compartment.

4.1.4 Inject halogen-containing sample by means of a gastight syringe, (typical sample loop volume: 160 µl).

4.1.5 After sample injection, monitor the transient signal at 520 nm.

METHOD 9c

(BROMINE)

(cont'd)

4.2 Calibration and standards.

Prepare standards from As Br_3 up to 100 ppm bromine, (concentrations larger than 100 ppm show deviation from linearity).

5. REFERENCE

Ramasamy, S.M., Jabbar, M.S.A., and Mottola, Horacio A. Anal Chem 52 2062 (1980).

METHOD 10

(CALCIUM OXIDE)

Method Ref:	10 NIOSH S205
Range:	2.6 to 10.16 mg/m^3
Precision:	$(\overline{CV}_T)$ 0.063
Procedure:	Filter collection acid digestion, atomic absorption.

1. APPARATUS

1.1 Sampling Equipment: Follow procedure outlined in Method 5.

1.2 Atomic absorption spectrophotometer, having a monochromator with a reciprocal linear dispersion of about 0.65 nm/mm in the ultra-violet region. The instrument must be equipped with an air-acetylene burner head.

1.2.1 Calcium hollow cathode lamp

1.2.2 Oxidant: compressed air

1.2.3 Fuel: acetylene

1.2.4 Pressure-reducing valves, a 2 gauge, 2 stage pressure reducing valve and appropriate hose connections are needed for each compressed gas tank used.

1.3 Glassware, borosilicate:

1.3.1 125 ml Phillips beakers with watchglass covers

1.3.2 Pipets, delivery or graduated, 1, 5, 10 ml

1.3.3 25 and 100 ml volumetric flasks

1.4 Adjustable thermostatically controlled hot plate capable of reaching 400°C.

2. REAGENTS

All reagents used must be ACS Reagent Grade or better.

2.1 Double distilled water

2.2 Concentrated nitric acid

2.3 Dilute hydrochloric acid (5 ml concentrated hydrochloric acid diluted to 100 ml with distilled or deionized water) containing 1% La (1 g La/100 ml).

2.4 Perchloric acid, 60% solution.

2.5 Commercially prepared aqueous standard stock solutions; 1000 µg/ml of calcium (1400 µg/ml calcium oxide).

3. PROCEDURE

3.1 Cleaning of Equipment

3.1.1 Before use, all glassware should initially be soaked in a mild detergent solution to remove any residual grease or chemicals.

3.1.2 After initial cleaning, glassware, must be cleaned with hot concentrated nitric acid and then rinsed thoroughly with tap water and distilled water, in that order, and then dried.

4. COLLECTION OF SAMPLES

Follow procedure outlined in Method 5.

4.1 A sample size of 85 litres is recommended. Sample at a flow rate of 1.5 litres per minute. The flow rate should be known with an accuracy of ±5%.

4.2 Analysis of Samples

4.2.1 Transfer each sample to a clean 125 ml Phillips beaker.

4.2.2 Wet Ashing. Treat the Sample in each beaker with 5 ml of concentrated nitric acid to destroy the filter. Cover each beaker with a watchglass and heat on a hot plate (140°C) in a fume hood until most of the acid has evaporated. Add 2 ml concentrated nitric acid and 1 ml 60% perchloric acid. Cover each beaker with a watchglass and heat it on a high temperature hot plate (100°C) in a perchloric acid fume hood until dense fumes of perchloric acid appear. Using distilled water, carefully rinse the material on the bottom of the watchglass into the beaker, rinse sides of beaker, and allow the solution to evaporate to dryness.

4.2.3 Cool each beaker and dissolve residues in 5 ml dilute hydrochloric acid containing 1% La. Calcium and its compounds are soluble in hydrochloric acid and no special precaution is needed to solubilize the calcium compounds.

4.2.4 Quantitatively transfer the clear solution to a 100 ml volumetric flask.

4.2.5 Rinse each beaker at least twice with 5 ml portions of dilute hydrochloric acid (containing 1% La) and quantitatively transfer each rinsing to the volumetric flask. Dilute all samples to 100 ml with dilute hydrochloric acid (containing 1% La).

4.2.6 Aspirate the solutions into an oxidizing air-acetylene flame and record the absorbance at 422.7 nm. The absorbance is proportional to the calcium oxide concentration and can be determined from the appropriate calibration curve.

4.2.7 Appropriate filter blanks must be analyzed in accordance with the total procedure.

5. CALIBRATION AND STANDARDS

5.1 Prepare at least four working standards to cover the range from 100 to 1500 µg/100 ml calcium from the 1000 µg/ml stock calcium standard solution (1.10 to 2100 µg/100 ml of calcium oxide). Make all standard solutions in dilute hydrochloric acid (containing 1% La). Prepare fresh working standards each day.

5.2 Aspirate each of the standards and record the absorptions.

5.3 Prepare a calibration curve by plotting on linear graph paper the absorbance versus the concentration of each standard in µg/100 ml of calcium oxide.

6. CALCULATIONS

6.1 Read the weight in µg, corresponding to the total absorbance from the standard curve. No volume corrections are needed, if the standard curve is based on µg/100 ml.

6.2 Correction for the blank must be made for each sample.

µg = µg sample - µg blank

6.3 Calculate the µg of calcium oxide by multiplying the "g" of calcium found by 1.40, which is a conversion factor to convert µg calcium to µg calcium oxide.

6.4 The concentration of calcium oxide in the air sample can be expressed in mg/m^3.

7. REFERENCES

1. Analytical Methods for Atomic Absorption Spectrophotometry, The Perkin-Elmer Corp., Norwalk, Connecticut, 1971.

2. Methods for Emission Spectrochemical Analysis, ASTM Committee E-2, Philadelphia, 1971.

3. Documentation of NIOSH Validation Tests, NIOSH Contract CDC-99-74-45.

METHOD 11

(CARBON DISULFIDE)

Method Ref:	11 NIOSH S248
Range:	14.7 to 58.8 ppm
Precision:	$(\overline{CV}_T)$ 0.059
Procedure:	Adsorption on charcoal, desorption with benzene, GC.

1. APPARATUS

1.1 A calibrated personal sampling pump.

1.2 Charcoal tubes: See Method 1a.

1.3 Drying tubes: glass tube with both ends open, 7 cm long with a 6 mm O.D. and a 4 mm I.D. To add the dessicant into the tube, a plug of silylated glass wool is placed into one end of the tube, and the tube is filled with 270 mg of granular anhydrous sodium sulfate. Another plug of silylated glass wool is placed over the sodium sulfate, and the tube is capped at both ends.

1.4 Gas chromatograph equipped with a flame photometric detector, with a sulfur filter.

1.5 Column (6 ft. x 1/4 in. O.D. glass) packed with 5% OV-17 on 80/100 mesh Gas Chrom Q.

1.6 An electronic integrator or some other suitable method for measuring peak areas.

1.7 Microlitre syringes: 10 microlitre, and other convenient sizes for preparing standards.

1.8 Pipets: 10 ml delivery pipets.

1.9 Volumetric flasks: 25 ml or convenient sizes for preparing standards solutions.

2. REAGENTS

2.1 Chromatographic quality carbon disulfide.

2.2 Benzene, reagent grade.

2.3 Purified oxygen.

2.4 Purified nitrogen.

2.5 Prepurified hydrogen.

2.6 Filtered compressed air.

3. PROCEDURE

3.1 Cleaning of Equipment. See Method 1a.

3.2 Calibration of Personal Pumps. See Method 1a.

3.3 Collection of Samples

3.3.1 At the ceiling OSHA standard concentration, a sample size of 6 litres is recommended. Sample for 30 minutes at a flow rate of 0.20 litres per minute.

3.3.2 At the 8 hour time weighted average OSHA standard, a sample size of 12 litres is recommended. Sample at a flow rate of 0.20 litres per minute.

3.3.3 It has been found that carbon disulfide tends to migrate within the charcoal tube from the front section to the backup section when held at ambient temperatures for prolonged periods of time. This migration can effectively be retarded by storing the samples at refrigerator temperatures. The tubes appear to be unaffected by short storage at elevated temperatures or by shipping under reduced pressures. It is recommended that the samples be refrigerated if sample analysis cannot be performed within one week.

3.4 Analysis of Samples

3.4.1 Preparation of Samples. See Method 1a.

3.4.2 Desorption of Samples. Prior to analysis, 10 ml of benzene is pipetted into each sample container.

3.4.3 GC Conditions. The typical operating conditions for the gas chromatograph are:

1. 20 ml/min nitrogen carrier gas flow
2. 150 ml/min hydrogen gas flow to detector
3. 35 ml/min air flow to detector
4. 20 ml/min oxygen gas flow to detector
5. 150°C injector temperature
6. 145°C detector temperature
7. 30°C column temperature

3.4.4 Injection. 5 µl - aliquot of sample is injected.

4. CALCULATIONS

4.1 Computed the same way as Method 1a.

4.2 Read the weight, in mg, corresponding to each peak area from the standard curve. No volume corrections are needed, if the standard curve is based on mg/10 ml benzene, and the volume of sample injected is identical to the volume of the standards injected.

5. REFERENCES

1. McCammon, C., Quinn, P., and Kupel, R., "A Charcoal Sampling Method and a Gas Chromatographic Analytical Procedure for Carbon Disulfide," Amer. Ind. Hyg. Assoc. J., 36, 618, August 1975.

2. Documentation of NIOSH Validation Test, NIOSH Contract CDC-99-74-45.

3. Final Report, NIOSH Contract HSM-99-71-31, "Personal Sampler Pump for Charcoal Tubes," Semptember 15, 1972.

METHOD 12

(CARBON TETRACHLORIDE)

Method Ref:	12 NIOSH S314
Range:	65 to 299 mg/m^3
Precision:	$(\overline{CV}_T)$ 0.092
Procedure:	Adsorption on charcoal, desorption with carbon disulfide, GC.

1. APPARATUS

1.1 A calibrated personal sampling pump.

1.2 Charcoal tubes: See Method 1a.

1.3 Gas chromatograph equipped with a flame ionization detector.

1.4 Column (20 ft. x 1/8 in. stainless steel) packed with 10% FFAP.

1.5 An electronic integrator or some other suitable method for measuring peak areas.

1.6 Two millilitre sample containers with glass stoppers or Teflon-lined caps. If an automatic sample injector is used, the associated vials may be used.

1.7 Microlitre syringes: 10 microlitre, and other convenient sizes for making standards.

1.8 Pipets: 1.0 ml, graduated in 0.1 ml increments.

1.9 Volumetric flasks; 10 ml or convenient sizes for making standard solutions.

2. REAGENTS

2.1 Chromatographic quality carbon disulfide.

2.2 Carbon Tetrachloride, reagent grade.

2.3 Decane, or other suitable internal standard.

2.4 Purified nitrogen.

2.5 Prepurified hydrogen.

2.6 Filtered compressed air.

METHOD 12

(CARBON TETRACHLORIDE)

(cont'd)

3. PROCEDURE

3.1 Cleaning of equipment. See Method 1a.

3.2 Calibration of Personal Pumps. See Method 1a.

3.3 Collection of Samples

3.3.1 For determining the ceiling and peak concentrations, a sample size of 5 litres is recommended. Sample for 5 minutes at a flow of 1.0 litre per minute. For determining the T.W.A. concentration, a sample size of 15 litres per minute or less. The flow rates should be known with an accuracy of at least $\pm$5%.

4. ANALYSIS OF SAMPLES

4.1 Preparation of Samples. See Method 1a.

4.2 Desorption of Samples. Prior to analysis, 1.0 ml of carbon disulfide is pipetted into each sample container. Desorption should be done for 30 minutes.

4.3 GC Conditions. The typical operating conditions for the gas chromatograph are:

1. 30 ml/min (60 psig) Nitrogen carrier gas flow
2. 30 ml/min (25 psig) Hydrogen gas flow to detector
3. 300 ml/min (60 psig) Air flow to detector
4. 155°C injector temperature
5. 200°C manifold temperature (detector)
6. 60°C column temperature

4.4 Injection. 5 µl - aliquot is injected.

5. CALCULATIONS

5.1 See Method 1a.

5.2 Read the weight, in mg, corresponding to each peak area from the standard curve. No volume corrections are needed, if the standard curve is based on mg per 1.0 ml carbon disulfide and the volume of sample injected is identical to the volume of the standards injected.

6. REFERENCES

1. Cadmium Dust, S312, Backup Data Report prepared under NIOSH Contract No. CDC-99-74-45, 1974-1976.

2. Christian, Gary, and Feldman, Fredric, Atomic Absorption Spectroscopy, Wiley-Interscience, N.Y., pp. 355-56, 1970.

3. Dennis, Richard, Ed., Handbook on Aerosols, Technical Information Center, Office of Public Affairs, U.S. Energy Research and Development Administration, 1976, pp. 2-3.

4. Memoranda, Kenneth A. Busch (Chief, Statistical Service, DLCD), to Deputy Director, DLCD, dated 6 January 1975, 8 November 1974, subject: "Statistical Protocol for Analysis of Data from Contract CDC-99-74-45."

5. S313 Backup Data Report for Cadmium Fume, prepared under NIOSH Contract No. 210-76-0123, 26 November 1976.

6. Analytical Methods for Atomic Absorption Spectrophotometry, The Perkin-Elmer Corporation, Norwalk, Conn., 1971.

7. Methods for Emission Spectrochemical Analysis, ASTM Committee E-2, Philadelphia, 1971.

METHOD 13

(CHLORINE)

Method Ref:	13 (P & CAM 209)
Range:	0.05 to 1.0 ppm
Precision:	± 5% (Analytical)
Procedure:	Fritted bubbler for samping, colorimetric methyl orange

1. APPARATUS

1.1 Spectrophotometer. Suitable for measurement at 505 nm, preferably accomodating 5 cm cells.

1.2 Fritted bubbler. Coarse porosity, of 250-350 ml capacity. A small bubbler of 50-60 ml capacity may be more convenient for industrial hygiene sampling; volumes of reagents are then reduced proportionally.

2. REAGENTS

Reagents must be ACS analytical grade quality. Distilled water should conform to ASTM Standard for Referee Reagent Water.

2.1 Chlorine-demand-free water. Add sufficient chlorine to distilled water to destroy the ammonia. The amount of chlorine required will be about ten times the amount of ammoniacal nitrogen present. In no case should the initial residual be less than 1.0 mg/l free chlorine. Allow the chlorinated distilled water to stand overnight or longer, then expose to direct sunlight for one day or until all residual chlorine is discharged. A UV lamp may also be used to discharge the chlorine.

2.2 Methyl orange stock solution, 0.05%. Dissolve 0.500 g reagent grade methyl orange in distilled water and dilute to 1 litre. This solution is stable indefinitely if freshly boiled and cooled distilled water is used.

2.3 Methyl orange reagent, 0.005%. Dilute 100 ml of stock solution to 1 litre with distilled water. Prepare fresh for use.

2.4 Sampling solution. 6 ml of 0.005% methyl orange reagent is diluted to 100 ml with distilled water and 3 drops (0.15 - 0.20 ml) of 5.0 N HCl added. One drop of butanol may be added to induce foaming and increase collection efficiency.

2.5 Acidified water. to 100 ml of distilled water, add 3 drops (0.15 - 0.20 ml) of 5 N HCl.

2.6 Potassium dichromate solution, 0.1000 N. Dissolve 4.905 g anhydrous $K_2Cr_2O_7$, primary standard grade, in distilled water and dilute to 1 litre.

2.7 Starch indicator solution. Prepare a thin paste of 1 g of soluble starch in a few ml of distilled water. Bring 200 ml of distilled water to a boil, remove from heat, and stir in the starch paste. Prepare fresh before use.

2.8 Potassium iodide, reagent grade.

2.9 Sodium thiosulfate solution, 0.1 N. Dissolve 25 g of $Na_2S_2O_3.5H_2O$ in freshly boiled and coooled distilled water and diulte to 2 litres. Add 5 ml chloroform as preservative and allow to age for 2 weeks before standardizing as follows: To 80 ml of distilled water, add, with constant stirring, 1 ml conc. H_2SO_4, 10.00 ml 0.1000 N $K_2Cr_2O_7$, and approximately 1 g of KI. Allow to stand in the dark for 6 minutes. Titrate with 0.1 N thiosulfate solution. Upon approaching the endpoint (brown colour changing to yellowish green), add 1 ml of starch indicator solution and continue titrating to endpoint (blue to light green).

$$\text{Normality } Na_2S_2O_3 = \frac{1.000}{\text{mls of } Na_2S_2O_3 \text{ used}}$$

2.10 Sodium thiosulfate solution, 0.01 N. dilute 100 ml of the aged and standardized 0.1 N $Na_2S_2O_3$ solution to 1 litre with freshly boiled and cooled distilled water. Add 5 ml chloroform as preservative and store in a glass-stoppered bottle. Standardize frequently with 0.1 N $K_2Cr_2O_7$.

2.11 Chlorine solution, approximately 10 ppm. Prepare by serial dilution of household bleach (approximately 50,000 ppm), or by dilution of strong chlorine water made by bubbling chlorine gas through cold distilled water. The diluted solution should contain approximately 10 ppm of free (available) chlorine.

3. PROCEDURE

3.1 Place 100 ml of sampling solution in a fritted bubbler. A measured volume of air is drawn through at a rate of 1-2 l/min. for a period of time appropriate to the estimated chlorine concentration. Transfer the solution to a 100 ml volumetric flask and make to volume, if necessary, with acidified water. Measure absorbance at 505 nm in 5 cm cells against distilled water as reference.

METHOD 13

(CHLORINE)

(cont'd)

4. CALIBRATION AND STANDARDS

4.1 Prepare a series of six 100 ml volumetric flasks containing 6 ml of 0.005% methyl orange reagent, 75 ml distilled water, and 3 drops (0.15-0.20 ml) of 5.0 N HCl. Carefully and accurately pipet 0, 0.5, 1.0, 5.0 and 9.0 ml of chlorine solution (approximately 10 ppm) into the respective flasks, holding the pipet tip beneath the surface. Quickly mix and make to volume with distilled water.

4.2 Immediately standarize the 10 ppm chlorine solution as follows: To a flask containing 1 gm KI and 5 ml glacial acetic acid, add 400 ml of chlorine solution, swirling to mix. Titrate with 0.01 N $Na_2S_2O_3$ until the iodine colour becomes a faint yellow. Add 1 ml of starch indicator solution and continue the titration to the end-point (blue to colorless). One ml of 0.0100 N $Na_2S_2O_3$ = 0.3546 mg of free chlorine. Compute the amounts of free chlorine added to each flask in 4.1.

4.3 Transfer the standards prepared in 4.1 to absorption cells and measure absorbance vs micrograms of chlorine to draw the standard curve.

5. CALCULATIONS

$$\text{ppm } Cl_2 = \frac{\text{mg}Cl_2 \text{ found}}{\text{Litres of air sampled}} \times \frac{24.450}{71}$$

For different temperatures and atmospheric pressures, proper correction for air volume should be made to standard conditions of 25°C and 760 Torr.

6. REFERENCES

1. Taras, M., "Colorimetric Determination of Free Chlorine with Methyl Orange", Anal Chem 19;3-12, 1947.

2. Boltz, D.F., Colorimetric Determination of Non-Metals, p. 163, Interscience Publishers, New York, 1958.

3. Standard methods for the Examination of Water and Waste Water, 12th Ed., p. 9, Americal Public Health Association, New York, 1965.

4. Traylor, P.A. and Shrader, S.A., Determination of Small Amounts of Free Bromine in Air, Dow Chemical Company, Main Laboratory Reference MR4N, Midland, Michigan.

5. Thomas, M.D. and Amtower, R., Unpublished work.

6. Intersociety Committee, Methods of Air Sampling and Analysis, Analysis of Free Chlorine Content of the Atmosphere, (42215-01-70T), pp. 282-284, American Public Health Association, Washington, D.C., 1972.

METHOD 14

(ORGANIC SOLVENTS)

Method Ref:	14 (P & CAM 127)
Range:	See Table 1
Precision:	10.5% RSD
Procedure:	Adsorption on charcoal, desorption with carbon disulfide, GC.

1. APPARATUS

1.1 Personal sampling pump.

1.2 Charcoal tubes: Similar to the ones specified in Method 1a.

1.3 Gas chromatograph equipped with a flame ionization detector.

1.4 Column (20 ft. x 1/8 in.) with 10% FFAP stationary phase on 80/100 mesh, acid-washed DMCS Chromosorb W solid support. Other columns capable of performing the required separations may be used.

1.5 A mechanical or electronic integrator or a recorder and some method for determining peak area.

1.6 Microcentrifuge tubes, 2.5 ml, graduated.

1.7 Hamilton syringes: 10 µl, and convenient sizes for making standards.

1.8 Pipets: 0.5 ml delivery pipets or 1.0 ml type graduated in 0.1 ml increments.

1.9 Volumetric flasks: 10 ml or convenient sizes for making standard solutions.

2. REAGENTS

2.1 Spectroquality carbon disulfide (Matheson, Coleman and Bell).

2.2 Sample of the specific compound under study, preferable chromatoquality grade.

2.3 Bureau of Mines Grade A helium.

2.4 Prepurified hydrogen.

2.5 Filtered compressed air.

3. PROCEDURE

3.1 Cleaning of Equipment: Follow procedure outlined in Method 1a.

3.2 Calibration of Pumps: Follow procedure outlined in Method 1a.

3.3 Collection of Samples: Follow procedure outlined in Method 1a.

3.3.1 The sample should be taken at a flow rate of 1.0 L/min or less. The minimum and maximum sample volumes that should be collected for each solvent are shown in Table 1.

3.4 Analysis of Samples

3.4.1 Preparation of Samples: Follow procedure oulined in Method 1a.

3.4.2 Desorption of Samples. Prior to analysis, one-half ml of carbon disulfide is pipetted into each test tube. Tests indicate that desorption is complete in 30 minutes if the sample is stirred occasionally during this period.

3.4.3 GC Conditions. The typical operating conditions for the gas chromatograph are:

1. 85 cc/min. (70 psig) helium carrier gas flow.
2. 65 cc/min. (24 psig) hydrogen gas flow to detector.
3. 500 cc/min. (50 psig) air flow to detector.
4. 200°C injector temperature.
5. 200°C manifold temperature (detector).
6. Isothermal oven or column temperature - refer to Table 1 for specific compounds.

4. CALCULATIONS

4.1 Results are computed in a similar manner as outlined in Method 1a.

4.2 The weight in mg, corresponding to each peak area is read from the standard curve for the particular compound. No volume corrections are needed, if the standard curve is based on mg/0.5 ml CS_2 and the volume if sample injected is identical to the volume of the standards injected.

5. REFERENCES

1. White, L.D., Taylor, D.G., Mauer, P.A., and Kupel, R.E., "A Convenient Optimized Method for the Analysis of Selected Solvent Vapors in the Industrial Atmosphere", Am. Ind. Hyg. Assoc. J. 31;225, 1970.

2. Young, D.M. and Crowell, A.D., Physical Adsorption of Gases, pp. 137-146, Butterworths, London, 1962.

3. Federal Register, 37:202:22139-22142, 18 October 1972.

4. NIOSH Contract HSM-99-72-98m Scott Reseach Laboratories, Inc., "Collaborative Testing of Activated Charcoal Sampling Tubes for Seven Organic Solvents", pp. 4-22, 4-27, 1973.

METHOD 14

(ORGANIC SOLVENTS)

TABLE 1

Organic Solvent	Detection Limit (mg/sample)	Sample Volume (liters) Minimum[a]	Maximum[b]	G.C. Column Temp (°C)	Molecular Weight
Benzene	0.01	0.5	55	90	78.1
Chloroform	0.10	0.5	13	80	119.0
Ethylene dichloride	0.05	1.0	12	90	99.0
Styrene	0.10	1.5	34	150	104.0
Tetrachloroethylene	0.06	1.0	25	130	166.0
Trichloroethylene	0.05	1.0	17	90	131.0
Toluene	0.01	0.5	22	120	92.1
Xylene	0.02	0.5	31	100	106.0
1,1,1-Trichloroethane	0.05	0.5	13	100	133.0

(a) Minimum volume, in liters, required to measure 0.1 times the OSHA standard.

(b) These are breathrough volumes calculated with data derived from a potential plot (11.2) for activated coconut charcoal. Concentrations of vapour in air at 5 times the OSHA standard (11.3) or 500 ppm, whichever is lower, 25°C, and 760 torr were assumed. These values will be as much as 50% lower for atmospheres of high humidity. The effects of multiple contaminants have not been investigated, but it is suspected that less volatile compounds may displace more volatile compounds (see 3.1 and 3.2).

METHOD 15

(CRESOL, ALL ISOMERS)

Method Ref:	15 (NIOSH S167)
Range:	10.54 to 42.2 mg/m^3
Precision:	$(\overline{CV}_T)$ 0.068
Procedure:	Adsorption on silica gel, desorption with acetone, GC.

1. APPARATUS

1.1 A calibrated personal sampling pump.

1.2 Silica Gel Tubes: See Method 1a.

1.3 Gas chromatograph equipped with a flame ionization detector.

1.4 Column (10 ft. x 1/8 in. I.D. stainless steel) packed with 10% FFAP on 80/100 mesh, acid washed DMCS Chromosorb W.

1.5 An electronic integrator or some other suitable method for measuring peak areas.

1.6 Two millilitre sample containers with glass stoppers or Teflon-lined caps. If an automatic sample injector is used, the associated vials may be used.

1.7 Microlitre syringes: 10 microlitre, and other convenient sizes for making standards.

1.8 Pipets: 1.0 ml delivery pipets.

1.9 Volumetric flasks: Convenient sizes for making standard solutions.

2. REAGENTS

2.1 Chromatographic quality acetone.

2.2 Cresol (all isomers) - prepare a standard mixture of the isomers by adding together 20 g of the ortho, 40 g of the meta, and 30 g of the para isomers and mix.

2.3 Prepurified hydrogen.

2.4 Filtered compressed air.

2.5 Purified nitrogen.

2.6 n-Hexane, reagent grade.

METHOD 15

(CRESOL, ALL ISOMERS)

(cont'd)

3. PROCEDURE

3.1 Cleaning of Equipment. See Method 1a.

3.2 Calibration of Personal Pumps. See Method 1a.

3.3 Collection of Samples.

3.3.1 See Method 1a & 1b. A sample size of 20 litres is recommended. Sample at a flow of 0.20 litres per minute or less. The flow rate should be known with an accuracy of at least $\pm$5%.

4. ANALYSIS OF SAMPLES

4.1 Preparation of Samples. See Method 1a.

4.2 Desorption of Samples. Prior to analysis, 1.0 ml of acetone is pipetted into each sample container. Desorption should be done for 30 minutes after occasional shaking.

4.3 GC Conditions. The typical operating conditions for the gas chromatograph are:

1. 50 ml/min (60 psing) nitrogen carrier gas flow.
2. 65 ml/min (24 psig) hydrogen gas flow to detector.
3. 500 ml/min (50 psig) air flow to detector.
4. 230°C injector temperature.
5. 250°C manifold temperature (detector).
6. 200°C column temperature.

4.4 Injection . 5.0 µl aliquot of sample is injected.

5. CALCULATIONS

5.1 See Method 1a.

5.2 Read the weight, in mg, corresponding to each combined peak area from the standard curve. No volume corrections are needed, if the standard curve is based on mg/1.0 ml acetone and the volume of sample injected is identical to the volume of the standards injected. Add the weights found in the front and backup sections to get the total weight in the sample.

6. REFERENCES

1. White, L.D., et al, "A Convenient Optimized Method for the Analysis of Selected Solvent Vapors in the Industrial Atmosphere", Amer. Ind. Hyg. Assoc. J., 31: 225 (1970).

2. Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.

3. Final Report, NIOSH Contract HSM-99-71-31, "Personal Sampler Pump for Charcoal Tubes", September 15, 1972.

METHOD 16

(ALIPHATIC AMINES)

Method Ref:	16 (P & CAM 221 or NIOSH S221)
Range:	1 to 2400 mg/m^3 in a 10 litre sample of air
Precision:	($\overline{CV}_T$) 0.03 methylamine at 300 mg/m^3
Procedure:	Adsorption on Silica gel; elution with acid; GC analysis.

The method may be used to determine a single aliphatic amine or to determine two or more amines in a single sample. The method may be applied to the following individual compounds:

Methylamine
Cyclohexylamine

1. APPARATUS

1.1 Air Sampling Equipment

1.1.1 Sorbent tubes. The sorbent tubes consit of Pyrex glass tubes 125 mm long and 8 mm i.d., packed with three separate sections of 45/60 mesh activated silica gel. The weights of the three sections of silica gel are, in order, 600, 150 and 150 mg; these tubes are designed for sample flow in either direction. Plugs of 100 mesh stainless steel screen are used to contain the silica gel sections.

1.1.2 Personal Sampling Pump. The personal pump should be capable of operation at a constant flow rate or 200 L/min for up to 8 hr.

1.2 Gas chromatograph with a flame ionization detector and linear temperature programming.

1.3 A 1.8 m by 4 mm silanized glass column packed with 60/80 mesh Chromosorb 103 (Johns-Manville), or equivalent.

1.4 A 15 cm by 4 mm silanized glass precolumn packed with 10 cm of 8/20 mesh Ascarite (Arthur H. Thomas Company), or equivalent, and fitted into the injection port. The precolum should be replaced when the precision of the analysis becomes poor.

1.5 Recorder with an electronic digital integrator or equivalent.

1.6 Glass-stoppered test tubes or flasks.

1.7 Glass syringes, 10.

1.8 Pipettes and volumentric flasks for preparation of standard solutions.

2. REAGENTS

2.1 Sulfuric acid, 1.0N.

2.2 Sodium hydroxide, 1.1N.

2.3 Aliphatic amines, highest purity available (for use as standards).

2.4 Helium, Bureau of Mines Grade A.

2.5 Hydrogen, prepurified.

2.6 Air, compressed and filtered.

3. PROCEDURE

3.1 Cleaning of Equipment. See Method 1a.

3.2 With sorbent tube in a vertical position, sample the air at 200 L/min for the desired period of time (02.5 to 8 hr.). The flow rate and sampling time, or the volume, must be measured as accurately as possible.

3.3 Analysis of Samples

3.3.1 Preparation of Samples. Remove and discard the stainless steel plugs and glass spacers and transfer each section of silica gel to a separate glass-stoppered test tube or flask. Analyze each section separately.

3.3.2 Desorption. Desorb the amines from the silica gel by adding 2ml of 1.0 N sulfuric acid to the 150 mg sections and 8 ml. to the 600 mg section. Shake the sample mixtures occasionally over a period of 1 hr.

3.3.3 Neutralization. Transfer a 0.5 aliquot to another container and add 0.5 ml. of 1.1N sodium hydroxide to make the solution alkaline and regenerate the free amines. An aliquot of this solution is then analyzed by gas chromatography.

3.3.4 Gas Chromatographic Conditions. Typical operating conditions for the gas chromatograph are as follows:

Helium carrier gas flow rate, 120cc/min.

Hydrogen gas flow rate to detector, 40cc/min.

Air flow rate to detector, 540cc/min.

Injection port temperature, 160°C.

Detector temperature, 190°C.

Column temperature, 115 to 180°C at 10°C/min.; hold for 10 min.

4. CALCULATIONS

4.1 From the calibration curve read the concentration of the amine corresponding to the average peak height measured. Multiply this concentration value by the volume of 1.0 N sulfuric acid used to desorb the amine from the silica gel (8ml for 600 mg of silica gel, or 2ml for 150 mg). The result is the weight of amine (in mg) in the silica gel section. Correct each value for the amount of amine found in the corresponding blank. Add the amounts of amine found in the front and backup sections of the same sample tube to obtain the total weight of amine in the air sample.

4.2 The concentration of the amine in air may be expressed in mg/m^3.

$$mg/m^3 = \frac{\text{weight (mg) of amine} \times 100\ m^3}{\text{volume of air sampled (L)}}$$

5. REFERENCES

1. Campbell, Evan E., Wood, G.O., and Anderson, R.G., "Development of Air Sampling Techniques," Los Alamos Scientific Laboratory, Progress Reports LA-5634-PR (June 1974), LA-5973-PR (July 1975), and LA-6057-PR (September 1975).

2. Andre, C.E., and Mosier, A.R., "Precolumn Inlet System for the Gas Chromatographic Analysis of Trace Quantities of Short-Chain Aliphatic Amines," Anal. Chem., 45, 1971 (1973).

3. Wood, G.O., and Anderson,R.G. "Development of Air Monitoring Techniques Using Solid Sorbents, "Los Alamos Scientific Laboratory, Progress Reports LA-6216-PR (February 1976) and LA-6513-PR (September 1976).

METHOD 17

(1,4-DICHLOROBENZENE)

Method Ref:	17 (NIOSH S281)
Range:	183.2 to 777 mg/m^3
Precision:	$(\overline{CV}_T)$ 0.052
Procedure:	Adsorption on charcoal, desorption with carbon disulfide, GC.

1. APPARATUS

1.1 A calibrated personal sampling pump.

1.2 Charcoal tubes: See Method 1a.

1.3 Gas Chromatograph equipped with a flame ionization detector.

1.4 Column (10 ft. x 1/8 in. I.D. stainless steel) packed with 10% FFAP on 80/100 mesh, acid washed DMCS Chromosorb W.

1.5 An electronic integrator or some other suitable method for measuring peak areas.

1.6 Two millilitre sample containers with glass stoppers or Teflon-lined caps. If an automatic sample injector is used, the associated vials may be used.

1.7 Microlitre syringes: 10 microlitre, and other convenient sizes for making standards.

1.8 Pipets: 1.0 ml delivery pipets.

1.9 Volumetric flasks: 10 ml or convenient sizes for making standard solutions.

2. REAGENTS

2.1 Chromatographic quality carbon disulfide.

2.2 p-Dichlorobenzene, reagent grade.

2.3 Acetone, reagent grade.

2.4 p-Dichlorobenzene standard solution. Weigh out 3.50 g of p-Dichlorobenzene into a small beaker and add approximately 7 ml of acetone. Warm the solution gently to dissolve the p-Dichlorobenzene. Quantitatively rinse the resulting solution into a 10 ml volumetric flasks and bring to volume with acetone.

2.5 Purified nitrogen.

2.6 Prepurified hydrogen.

2.7 Filtered compressed air.

3. PROCEDURE

3.1 Cleaning of Equipment. See Method 1a.

3.2 Calibration of Personal Pumps. See Method 1a.

3.3 Collection of Samples

3.3.1 See Method 1a. A sample size of 3 litres is recommended. Sample at a flow rate of 0.05 litres per minute or less. The flow rate should be known with an accuracy of at least $\pm$ 5%.

3.4 Analysis of Samples

3.4.1 Preparation of Samples. See Method 1a.

3.4.2 Desorption of Samples. Prior to analysis, 1.0 ml of carbon disulfide is pipetted into each sample container. Desorption should be done for 30 minutes, with occasional shaking.

3.4.3 GC Conditions. The typical operating conditions for the gas chromatograph are:

1. 50 ml/min (60 psig) nitrogen carrier gas flow.
2. 65 ml/min (24 psig) hydrogen gas flow to detector.
3. 500 ml/min (50 psig) air flow to detector.
4. 225°C injector temperature.
5. 275°C manifold temperature (Detector).
6. 140°C column temperature.

3.4.4 Injection. A 5.0 µl aliquot is injected.

4. CALCULATIONS

4.1 See Method 1a. Read the weight, in mg, corresponding to each peak area from the standard curve. No volume corrections are needed, if the standard curve is based on mg/1.0 ml carbon disulfide, and the volume of sample injected is identical to the volume of the standards injected.

5. REFERENCES

1. White, L.D., et al, "A Convenient Optimized Method for the Analysis of Selected Solvent Vapors in the Industrial Atmosphere," Amer. Ind. Hyg. Assoc. J., 31: 225 (1970).

2. Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.

3. Final Report, NIOSH contract HSM-99-71-31, "Personal Sampler Pump for Charcoal Tubes," 15 Sepetemer 1972.

METHOD 18

(DICHLOROMETHANE - METHYLENE CHLORIDE)

Method Ref:	18 (NIOSH S329)
Range:	1700 to 7100 mg/m^3
Precision:	$(\overline{CV}_T)$ 0.073
Procedure:	Adsorption on charcoal, desorption with carbon disulfide, GC.

1. APPARATUS

1.1 A calibrated personal sampling pump.

1.2 Charcoal tubes: See Method 1a.

1.3 Gas chromatograph equipped with a flame ionization detector.

1.4 Column (20 ft. x 1/8 in. I.D. stainless steel) packed with 10% FFAP stationary phase on 100/120 mesh Supelcoport.

1.5 An electrostatic integrator or some other suitable method for measuring peak areas.

1.6 Two millilitre sample containers with glass stoppers or Teflon-lined caps. If an automatic sample injector is used, the associated vials may be used.

1.7 Microlitre syringes: 10 microlitre, and other convenient sizes for making standards.

1.8 Pipets: 1.0 ml graduated in 0.1 ml increments.

1.9 Volumetric flasks: 10 ml or convenient sizes for making standard solutions.

2. REAGENTS

2.1 Chromatographic quality carbon disulfide.

2.2 Methylene Chloride, reagent grade.

2.4 Purified nitrogen.

2.5 Prepurified hydrogen.

2.6 Filtered compressed air.

METHOD 18

(DICHLOROMETHANE - METHYLENE CHLORIDE)

(cont'd)

3. PROCEDURE

3.1 Cleaning of equipment. See Method 1a.

3.2 Calibration of Personal Pumps. See Method 1a.

3.3 Collection of Samples

3.3.1 See Method 1a. For determining the ceiling and peak concentrations, a maximum sample size of 1.0 litre is recommended. Sample for 5 minutes at a flow of 0.2 litres per minute. For determining the TWA concentration, a sample size of 2.2 litres is recommended; sample at a flow of 0.05 litres per minute or less. The flow rates should be known with an accuracy of at least $\pm$ 5%.

4. ANALYSIS OF SAMPLES

4.1 Preparation of Samples. See Method 1.

4.2 Desorption of Samples. Prior to analysis, 1.0 ml of carbon disulfide is pipetted into each sample container. Desorption should be done for 30 minutes after occasional shaking.

4.3 GC Conditions. The typical operating conditions for the gas chromatograph are:

1. 30 ml/min (60 psig) Nitrogen carrier gas flow.
2. 35 ml/min (25 psig) Hydrogen gas flow to detector.
3. 400 ml/min (60 psing) Air flow to detector.
4. 225°C injector temperature.
5. 250°C manifold temperature (detector).
6. 60°C column temperature.

4.4 Injection. A 5 µl aliquot is injected. An automatic sample injector can be used if it is shown to give reproducibility at least as good as the solvent flush technique.

5. CALCULATIONS

5.1 See Method 1a. Read the weight, in mg, corresponding to each peak area from the standard curve. No volume corrections are needed, if the standard curve is based on mg per 1.0 ml carbon disulfide and the volume of sample injected is identical to the volume of the standards injected.

5.2 A similar procedure is followed for the backup sections.

5.3 Add the amounts present in the front and backup sections of the same sample tube to determine the total weight in the sample.

6. REFERENCES

1. White,L.D., et al, "A Convenient Optimized Method for the Analysis of Selected Solvent Vapors in the Industrial Atmosphere," Amer. Ind. Hyg. Assoc. J., 31: 225 (1970).

2. Documentation of NIOSH Validation Test, NIOSH Contract No. CDC-99-74-45.

3. Final Report, NIOSH Contract HSM-99-71-31, "Personal Sampler Pump for Charcoal Tubes," 15 September 1972.

METHOD 19

(2,4-DICHLOROPHENOXYACETIC ACID)

Method Ref:	19 (NIOSH S279) 2,4-D
Range:	5.1 to 20.3 mg/m^3
Precision:	$(\overline{CV}_T)$: 0.051
Procedure:	Filter collection, methanol extraction, HPLC.

1. APPARATUS

1.1 Filter Unit. The filter unit consists of a 37 mm diameter glass fiber filter (Gelman Type AE or equivalent) and a 37 mm polystyrene two-piece cassette filter holder. The filter is held in the two-piece holder, supported by a backup pad. Secure the cassette holder together with tape or shrinkable band.

1.2 Personal Sampling Pump. A calibrated personal sampling pump.

1.3 Manometer.

1.4 Thermometer.

1.5 High pressure liquid chromatograph equipped with a variable wave-length U.V. detector set at 284 nm and a sample injection valve with a 50 microlitre external sample loop.

1.6 HPLC column packed with Zipax SAX (50 cm x 2 mm I.D. stainless steel). This column packing can be obtained from DuPont.

1.7 Filtration unit for protection of the HPLC from particulate filter fibers: Swinny stainless (13 mm) fitted with 13 mm diameter, 5 μ pore size Teflon filters. The filter can be obtained from Millipore.

1.8 An electronic integrator or some other suitable method for measuring peak areas.

1.9 Tweezers.

1.10 Syringes: 20 ml luer-lock.

1.11 Scintillation vials: 20 ml.

1.12 Volumetric flasks: Convenient sizes for preparing standard solutions.

1.13 Pipets: 15 ml and other convenient sizes for preparing standard solutions.

METHOD 19

(2,4-DICHLOROPHENOXYACETIC ACID)

(cont'd)

2. REAGENTS

Whenever possible, all reagents used must be ACS reagent grade or better.

2.1 2,4-Dichlorophenoxyacetic acid.

2.2 Methanol.

2.3 LC eluant, 0.001 N each of $NaClO_4$ and $Na_2B_4O_7$: Add 0.122 g $NaClO_4$ and 0.381 g $Na_2B_4O_7$. 10 H_2O together in a 1 litre volumetric flask. Bring to volume with distilled water. Mix thoroughly and filter the solution. Degas prior to use.

2.4 Standard 2,4-D solution: Prepare a 400 g/ml standard solution of 2,4-D in methanol by dissolving 400 mg of 2,4-D in methanol in a 1 litre volumetric flask and making to volume.

2.5 Compressed air or nitrogen for drying syringes.

3. PROCEDURE

3.1 Cleaning of Equipment. See Method 1a.

3.2 Collection of Samples

3.2.1 Assemble the filter in the two-piece filter cassette holder and close firmly. The filter is supported by a backup pad. Secure the cassette holder together with tape or shrinkable band.

3.2.2 Remove the cassette plugs and attach the outlet of the filter cassette to the personal sampling pump inlet with flexible tubing.

3.2.3 Air being sampled should not pass through any hose or tubing before entering the filter cassette.

3.2.4 A sample size of 100 litres is recommended. Sample at a flow rate of 1.0-1.5 litres/minute. The flow rate should be known with an accuracy of $\pm$5%.

3.3 Analysis of Samples

3.3.1 Remove the filter from the cassette with clean tweezers and place it in a 20 ml scintillation vial.

3.3.2 Add 15 ml of methanol and mix the solution by swirling. Allow the samples to stand for at least 0.5 hr. prior to filtration and analysis.

3.3.3 Connect a filtration unit fitted with a 13 mm Teflon filter to a clean 20 ml luer-lock syringe. Place the filtration end to a clean empty scintillation vial and remove the plunger of the syringe. Pour the sample into the open end of the syringe and reinsert the plunger. Flush the sample into the clean vial. The syringe/filtration system should be cleaned after filtration of each sample. To clean the assembly, it is not necessary to disassemble it. Back-flush the assembly by squirting methanol through the filter to remove the particulate material. Remove the plunger and thoroughly rinse the plunger and barrel. Blow dry the assembly with filtered nitrogen or air. The Teflon filter should be replaced periodically.

3.3.4 HPLC Conditions. The typical operating conditions for the high pressure liquid chromatograph are:

Column Temperature: Ambient
Column Pressure: 1000 psi
Flow Rate: 1.7 ml/minute
Mobile Phase: 0.001 N each of $NaClO_4$ and $Na_2B_4O_7$
Detector: U.V. at 284 nm
Capacity Ratio: 7.3

Under the above conditions, the 2,4-D peak will include the free acid and salt forms. If large amounts of esters are known to be present, the addition of a precolumn may be necessary.

3.3.5 Injection. The chromatograph is fitted with a sample injection valve and a 50 microlitre sample loop. Flush this loop thoroughly with the sample (500 microlitres), and inject the sample. The syringe should be rinsed and dried before the injection of another sample.

4. CALIBRATION AND STANDARDIZATION

4.1 From the stock standard solution (Section 2.4) appropriate aliquots are withdrawn and dilutions are made in methanol. Prepare at least 5 working standards to cover the range of 6.7 to 200 micrograms/ml. This range is based on a 100 litre sample.

4.2 Analyze samples as per Section 3.3. These samples need not be filtered.

4.3 Prepare a standard calibration curve by plotting concentration of 2,4-D in mg/15 ml versus peak area.

5. CALCULATIONS

See Method 1a.

5.1 Read the weight in mg, corresponding to each peak area from the standard curve. No volume correction is needed, if the standard curve is based on mg/15 ml methanol and the volume of sample injected is identical to the volume of the standards injected.

6. REFERENCES

1. Documentation of NIOSH Validation Tests, National Institute for Occupational Safety and Health, Cincinnati, Ohio (DHEW-NIOSH Publication #77-185), 1977. Available from Superintendent of Documents, U.S. Government Printing Office, Washington, D.C., Order No. 017-033-00231-2.

2. Backup Data Report for 2,4-D prepared under NIOSH Contract No. 210-76-0123.

METHOD 20

(p,p1-DIPHENYLMETHANE DIISOCYANATE (MDI) IN AIR)

Method Ref:	20 (NIOSH 142)
Range:	0.007-0.073 ppm
Precision:	Unknown
Procedure:	Colorimetric

1. APPARATUS

1.1 Sampling Equipment. The sampling unit for personal samples by the impinger collection method consists of the following components:

1.1.1 A midget impinger containing the absorbing solution or reagent.

1.1.2 Battery operated personal sampling pump - MSA Model G or equivalent. The samping pump is protected from splashover or water condensation by an adsorption tube loosely packed with a plug of glass wool and inserted between the exit arm of the impinger and the pump.

1.1.3 An integrating volume meter such as a dry gas or wet test meter.

1.1.4 Thermometer.

1.1.5 Manometer.

1.1.6 Stopwatch.

1.1.7 Various clips, tubing, spring connectors, and belt for connecting sampling apparatus to worker being sampled.

1.2 Beckman Model B spectrophotometer or equivalent.

1.3 Cells, 5 cm matched quartz cells.

1.4 Volumetric flasks (several of each): 100 ml and 1 litre.

1.5 Balance capable of weighing to at least three places, preferably four places.

1.6 Pipets, delivery: 0.5, 1, 2, 5, 10, 15 ml
graduated: 2 ml

1.7 Graduated cylinders: 50, 100 ml

METHOD 20

(p,p1-DIPHENYLMETHANE DIISOCYANATE (MDI) IN AIR)

(cont'd)

2. REAGENTS

All reagents must be made using ACS reagent grade or a better grade.

2.1 Double distilled water.

2.2 Sodium nitrite.

2.3 Sodium bromide.

2.4 Sulfamic acid.

2.5 Concentrated hydrochloric acid, 11.7N.

2.6 Glacial acetic acid, 17.6N.

2.7 N-(1-Naphthyl)-ethylenediamine dihydrochloride.

2.8 Sodium carbonate.

2.9 Methylene Dianiline (MDA).

2.10 Sodium Nitrite - Sodium Bromide Solution: Dissolve 3.0 g sodium nitrite and 5.0 g sodium bromide in double distilled water and dilute to 100 ml. The solution may be stored in the refrigerator for one week.

2.11 Sulfamic Acid Solution, Dissolve 10.0 g sulfamic acid in 100 ml double distilled water.

2.12 Absorbing Solution. Add 35 ml concentrated hydrochloric acid and 22 ml glacial acetic acid to about 600 ml double distilled water.

2.13 Coupling Solution. Dissolve 0.1 g N-(1-Naphthyl)-ethylenediamine dihydrochloride in 50 ml water, add 2 ml concentrated hydrochloric acid and dilute to 100 ml with double distilled water. This solution is stable for about ten days.

2.14 Sodium Carbonate. Dissolve 16.0 g sodium carbonate in double distilled water and dilute to 100 ml.

2.15 Solution A. Dissolve 0.23 g MDA in 700 ml glacial acetic acid. Dilute to 1 litre with double distilled water. This is equivalent to 300 mg MDI/1.

2.16 Solution B. Immediately after making solution A, pipet 10 ml solution A into a 1 litre volumetric flask. Add 35 ml concentrated hydrochloric acid, 15 ml glacial acetic acid, dilute to volume with double distilled water. This solution contains the equivalent of 3 µg MDI/ml.

3. PROCEDURE

3.1 Cleaning of Equipment. See Method 1a.

3.2 Collection of Samples

3.2.1 Pipet 15 ml of the absorbing solution into the midget impinger.

3.2.2 Connect the impinger (via the absorption tube) to the personal sampling pump with a short piece of flexible tubing. The minimum amount of tubing should be used between the sampling zone and impinger.

3.2.3 Turn on pump to begin sample collection. Care should be taken to measure the flow rate, time and/or volume as accurately as possible. Record atmospheric pressure and temperature. The sample should be taken at a flow rate of 1.0 L/min. Sample for 20 minutes making the final volume 20 litres.

3.2.4 After sampling, the impinger stem can be removed and cleaned. Tap the stem gently against the inside wall of the impinger bottle to recover as much of the sampling solution as possible. Wash the stem with a small amount (1-2 ml) of unused absorbing solution and add the wash to the impinger. Then the impinger is sealed with a hard, non-reactive stopper (preferably Teflon or glass).

3.3 Analysis of Samples

3.3.1 Remove the bubbler tube, if it is still attached, taking care not to remove any absorbing solution.

3.3.2 Start reagent blank at this point by adding 15 ml fresh absorbing solution to a clean bubbler cylinder.

3.3.3 To each cylinder, add 0.5 ml sodium nitrite solution, stir well, and allow to stand for 2 minutes.

3.3.4 Add 1 ml 10% sulfamic acid solution, stir for 30 seconds, and allow to stand for 2 minutes.

3.3.5 Add 1.5 ml sodium carbonate solution and stir.

3.3.6 Add 1 ml coupling solution and stir. Allow color to develop for 15 to 30 minutes.

3.3.7 Transfer each solution to a 5 cm quartz cell.

3.3.8 Using the blank, adjust the spectrophotometer to 0 absorbance at 555 nm.

3.3.9 Determine the absorbance of each sample at 555 nm.

4. CALIBRATION AND STANDARDS

4.1 To a series of five impinger cylinders, add the following amounts of absorbing solution: 15.0, 14.5, 14.0, 13.0, 10.0 ml respectively.

4.2 To the cylinder add standard solution B in the same order as the absorbing solution was added: 0.0, 0.5, 1.0, 2.0, 5.0 ml, so that the final volume is 15 ml (i.e. 0.0 ml of standard is added to the 15 ml absorbing solution: 0.5 ml of standard is added to the 14.5 absorber solution, etc.). The cylinders now contain an amount of MDA equivalent to 0.0, 1.5, 3.0, 610, 15 g MDI, respectively. The standard containing 0.0 ml standard solution is a blank.

4.3 To each cyliner, add 0.5 ml sodium nitrite solution, stir well and allow to stand for 2 minutes.

4.4 Add 1 ml of 10% sulfamic acid solution, stir for 30 seconds, and allow to stand for 2 minutes.

4.5 Add 1.5 ml sodium carbonate solution and stir.

4.6 Add 1 ml coupling solution and stir. Allow color to develop for 15 to 30 minutes.

4.7 Transfer each solution to a 5 cm quartz cell.

4.8 Using the balnk, adjust the spectrophotometer to 0 absorbance at 555 nm.

4.9 Determine the absorbance of each standard at 555 nm.

4.10 A standard curve is constructed by plotting the absorbance against micrograms MID.

5. CALCULATIONS

5.1 Blank values if any, should first be substracted from each sample.

5.2 From the calibration curve, read the micrograms MDI corresponding to the absorbance of the sample.

5.3 Calculate the concetration of MDI in the air sampled in ppm, defined as 1 MDI per litre of air.

$$ppm = \frac{g}{V_s} \times \frac{24.45}{MW}$$

Where:

ppm = parts per million MDI

g = micrograms MDI (Section 5.2)

V_s = corrected volume of air (Section 5.4)

24.45 = molar volume of an ideal gas at 25°C and 760 mm Hg

MW = Molecular weight of MDI, 250.27

5.4 Correct the volume of air sampled to standard conditions of 25°C and 760 mm Hg:

$$V_s = V \times \frac{P}{760} \times \frac{298}{T + 273}$$

Where:

V_s = volume of air in litres at 25°C and 760 mm Hg

V = volume of air in litres as measured

P = Barometric Pressure in mm Hg

T = Temperature of air in degree centigrade

6. REFERENCE

Grim, K.E., and Linch, A.L., "Recent Isocyanate-in-Air Analysis Studies," American Industrial Hygiene Association Journal, 25, 285 (1964).

METHOD 21a

(EPICHLOROHYDRIN)

Method Ref:	21a (NIOSH S118
Range:	11.7 to 43.1 mg/m^3
Precision:	$(\overline{CV}_T)$ 0.057
Procedure:	Adsorption on charcoal, desorption with carbon disulfide, GC

1. APPARATUS

1.1 A calibrated personal sampling pump.

1.2 Charcoal tubes: See Method 1a.

1.3 Gas chromatograph equipped with a flame ionization detector.

1.4 Column (10 ft x 1/8 in stainless steel) packed with 10% FFAP on 80/100 mesh, acid washed DMCS Chromosorb W.

1.5 An electronic integrator or some other suitable method for measuring peak areas.

1.6 Two millilitre sample containers with glass stoppers or Teflon-lines caps. If an automatic sample injector is used, the associated vials may be used.

1.7 Microlitre syringes: 10 microlitre, and other convenient sizes for making standards.

1.8 Pipets: 1.0 millilitre delivery pipets.

1.9 Volumetric flasks: 10 millilitre or convenient sizes for making standard solutions.

2. REAGENTS

2.1 Chromatographic quality carbon disulfide.

2.2 Epichlorohydrin, reagent grade.

2.3 Purified nitrogen.

2.4 Prepurified hydrogen.

2.5 Filtered compressed air.

3. PROCEDURE

3.1 Cleaning of Equipment. See Method 1a.

3.2 Calibration of Personal Pumps. See Method 1a.

3.3 Collection of Samples. See Method 1a.

3.3.1 A sample size of 20 litres is recommended. Sample at a flow of 0.20 litre per minute or less. The flow rate should be known with an accuracy of at least $\pm$ 5%.

3.4 Analysis of Samples.

3.4.1 Preparation of Samples. See Method 1a.

3.4.2 Desorption of Samples. Prior to analysis, 1.0 ml of carbon disulfide is pipetted into each sample container. Desorption should be done for 30 minutes with occasional shaking.

3.4.3 GC Conditions. The typical operating conditions for the gas chromatograph are:

1. 50 ml/min (60 psig) nitrogen carrier gas flow
2. 65 ml/min (24 psig) hydrogen gas flow to detector
3. 500 ml/min (50 psig) air flow to detector
4. 175°C injector temperature
5. 215°C manifold temperature (detector)
6. 120°C column temperature

3.4.4 Injection. A 5µl aliquot is injected.

4. CALCULATIONS

See Method 1a.

4.1 Read the weight, in mg, corresponding to each peak area from the standard curve. No volume corrections are needed if the standard curve is based on mg/1.0 ml carbon disulfide and the volume of sample injected is identical to the volume of the standards injected.

5. REFERENCES

5.1 White, L.D., et al, "A Convenient Optimized Method for the Analysis of Selected Solvent Vapors in the Industrial Atmosphere", American Industrial Hygienists Association J., 31: 225 (1970).

5.2 Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.

5.3 Final Report, NIOSH Contract HSM-99-71-31, "Personal Sampler Pump for Charcoal Tubes", 15 September 1972.

METHOD 21b

(EPICHLOROHYDRIN)

Method Ref:	21b
Range:	Unknown
Precision:	Unknown
Procedure:	Collection on Fluorosil tubes, determination by gas chromatography - mass fragmentography

1. APPARATUS

1.1 Finnigan 4000 gas chromatograph - mass spectrometer or equivalent.

1.2 Glass column, 1.5 m x 0.3 mm i.d. packed with 80/100 mesh Carbopack C, loaded with 0.2% Carbowax 1500.

1.3 All-glass separator.

1.4 Vacuum diverter system to prevent the solvent contaminating the source of the mass spectrometer.

2. REAGENTS

All reagents must be analytical grade.

2.1 Diethyl ether.

2.2 Epichlorohydrin.

3. PROCEDURE

3.1 Fluorosil tubes are used.

3.2 Samples are desorbed in diethyl ether.

3.3 1 or 5 µl of sample are injected 100°C (isothermal); carrier gas (helium) flow rate 20 ml/min.

3.4 Mass spectrometer operated in electron impact mode with multiple ion detection unit tuned at m/e 49.

4. CALIBRATION AND STANDARDS

Prepare standard solutions of EPCH in diethyl ether.

METHOD 21b

(EPICHLOROHYDRIN)

(cont'd)

5. CALCULATIONS

5.1 Read concentrations of epichlorohydrin from analytical curve.

5.2 Correct for blank values.

5.3 Convert result to mg/m^3.

6. REFERENCE

Van Lierop, J.B.H., J. of Chrom. 166 609 (1978).

METHOD 22

(ETHYLBENZENE)

Method Ref:	22(NIOSH S29)
Range:	222 to 884 mg/m^3
Precision:	$(\overline{CV}_T)$ 0.041
	Adsorption on charcoal, desorption with carbon disulfide, G.C.

1. APPARATUS

1.1 An approved and calibrated personal sampling pump.

1.2 Charcoal tubes. See Method 1a.

1.3 Gas chromatograph equipped with a flame ionization detector.

1.4 Column (10 ft x 1/8 in. I.D. stainless steel) packed with 10% FFAP on 80/100 mesh, acid washed DMCS Chromosorb W.

1.5 An electronic integrator or some other suitable method for measuring peak areas.

1.6 One millilitre sample containers with glass stoppers or Teflon-lined caps.

1.7 Microlitre syringes: 10 µl, and other convenient sizes for making standards.

1.8 Pipets: 0.5 ml delivery pipets or 1.0 ml type graduated in 0.1 ml increments.

1.9 Volumetric flasks: 10 ml or convenient sizes for making standard solutions.

2. REAGENTS

2.1 Chromatographic quality carbon disulfide.

2.2 Ethyl benzene, reagent grade.

2.3 Purified nitrogen.

2.4 Prepurified hydrogen.

2.5 Filtered compressed air.

3. PROCEDURE

3.1 Cleaning of Equipment. See Method 1a.

3.2 Calibration of Personal Pumps. See Method 1a.

3.3 Collection of Samples.

3.3.1 See Method 1a.

A maximum sample size of 10 litres is recommended. Sample at a flow of 0.20 litres per minute or less. The flow rate should be known with an accuracy of at least $\pm$ 5%.

3.4 Analysis of Samples.

3.4.1 Preparation of Samples. See Method 1a.

3.4.2 Desorption of Samples. Prior to analysis, 0.5 ml of carbon disulfide is pipetted into each sample container. Tests indicate that desorption is complete in 30 minutes if the sample is stirred occasionally during this period.

3.4.3 GC Conditions. The typical operating conditions for the gas chromatograph are:

1. 50 cc/min (60 psig) nitrogen carrier gas flex
2. 65 cc/min (24 psig) hydrogen gas flex to detector
3. 500 cc/min (50 psig) air flow to detector
4. 195°C injector temperature
5. 250°C manifold temperature (detector)
6. 85°C column temperature

4. CALCULATIONS

4.1 Read the weight in mg corresponding to peak area from standard curve. Results are computed in a similar manner to Method 1a.

4.2 A similar procedure is followed for the backup sections.

4.3 Add the weights found in the front and backup sections to get the total weight in the sample.

5. REFERENCES

5.1 White, L.D., et al, "A Convenient Optimized Method for the Analysis of Selected Solvent Vapors in the Industrial Atmosphere", American Industrial Hygienists Association. J., 31: 225 (1970)

5.2 Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.

5.3 Final Report, NIOSH Contract HSM-99-71-31, "Personal Sampler Pump for Charcoal Tubes", 15 September 1972.

METHOD 23

(ETHYL CHLORIDE)

Method Ref:	23(NIOSH S105)
Range:	1590 to 6500 mg/m^3
Precision:	$(\overline{CV}_T)$ 0.096
Procedure:	Adsorption of charcoal, desorption with carbon disulfide, GC/FID

1. APPARATUS

1.1 Sampling Equipment

1.1.1 A calibrated personal sampling pump.

1.1.2 Sampling Tubes. The sampling train consists of two separate charcoal tubes connected in series. The tubes are glass tubes with both ends flame-sealed, 10 cm long with an 8 mm o.d. and a 6 mm i.d. The front tube contains 400 mg of 20/40 mesh activated coconut charcoal; the backup tube, 200 mg.

1.1.3 Thermometer.

1.1.4 Barometer.

1.1.5 Stopwatch.

1.2 Gas chromatograph equipped with a flame ionization detector.

1.3 Column, 20 ft x 1/8 in. I.D. stainless steel packed with 10% FFAP stationary phase on 100/120 mesh Supelcoport.

1.4 An electronic integrator of some other suitable method for measuring peak areas.

1.5 Glass serum vials for desorption, 3 ml, molded to take 13 mm rubber septa and 13 mm aluminum seals.

1.5.1 Rubber septa, 13 mm.

1.5.2 Lacquered aluminum seals or caps, 13 mm

1.5.3 Hand crimper, 13 mm, or equivalent for properly sealing the vial assembly.

Note: Glass stoppered containers are not adequate because of significant sample losses during desorption.

1.6 Microlitre syringes: 500 µl and other convenient sizes for making internal standard stock solution.

1.7 Gas-tight syringes: 10 ml and other convenient sizes for making standards.

1.8 Syringe: 5.0 ml capacity for adding the carbon disulfide used for desportion.

1.9 Syringe needle: 1.5 in, 22 gauge or other convenient size.

2. REAGENTS

All reagents must be ACS reagent grade or better.

2.1 Carbon disulfide, chromatographic quality.

2.2 Ethyl chloride, 99.7%.

2.3 Nonane or other suitable internal standard. The appropriate solution of the internal standard is prepared in carbon disulfide.

2.4 Purified nitrogen.

2.5 Prepurified hydrogen.

2.6 Filtered compressed air.

3. PROCEDURE

3.1 Cleaning of Equipment. See Method 1a.

3.2 Calibration of Personal Pumps. See Method 1a.

3.3 Collection of Samples.

3.3.1 See Method 1a.

A sample size of 3 litres is recommended. Sample at a flow rate of 0.05 litres per minute. The flow rate should be known with an accuracy of at least $\pm$ 5%.

3.4 Analysis of Samples.

3.4.1 Preparation of Samples. See Method 1a.

3.4.2 Desorption of Sample. Immediately before desorption, lift up or remove the removeable portion of the aluminum cap to expose a portion of the septum without destroying the seal. Insert a syringe needle through the septum keeping the tip of the needle just below the surface of the septum in the vial. (This needle serves as a vent to prevent pressure build-up in the vial when carbon disulfide is added.) Add 2.0 ml of carbon disulfide or 2.0 ml of internal standard stock solution into the sample-containing vial with the aid of a syringe. After the carbon disulfide addition, remove the needle being used as a vent.

3.4.3 GC Conditions. The typical operating conditions for the gas chromatograph are:

1. 30 ml/min (60 psig) nitrogen carrier gas flow
2. 30 ml/min (25 psig) hydrogen gas flow to detector
3. 300 ml/min (60 psig) air flow to detector
4. 160°C injector temperature
5. 190°C manifold temperature (detector)
6. 110°C column temperature

3.4.4 Injection of Sample. A 5 µl aliquot of the sample solution is injected into the gas chromatograph.

4. CALIBRATION AND STANDARDS

4.1 Seal a 3 ml serum vial, using a rubber septum and aluminum cap with the aid of a crimper.

4.2 Insert a syringe needle through the septum keeping the tip just below the surface of the septum, in order to provide a vent. With the aid of a syringe, inject 2.0 ml of carbon disulfide (or 2.0 ml of internal standard solution) into the vial. Remove the needle used as a vent.

4.3 Immediately before adding the ethyl chloride gas, withdraw an amount of air from the sealed vial equal to the volume of the gas to be added. Label and weigh the vial and record the weight. an appropriate amount of ethyl chloride is bubbled slowly into the carbon disulfide using a gas-tight syringe. The syringe needle should be immersed in the carbon disulfide during discharge of the ethyl chloride from the syringe.

4.4 The vial is weighed again and the weight (mg) of the ethyl chloride is calculated by taking the difference between the weight before and after the addition of ethyl chloride gas.

4.5 The concentration of standards can be expressed in terms of mg ethyl chloride per 2 ml of carbon disulfide. This unit is convenient because samples are desorbed in 2 ml of carbon disulfide.

4.6 A series of standards, varying in concentration over the range of interest, are prepared as described above and analyzed under the same GC conditions and during the same time period as the unknown samples. Curves are established by plotting concentration in mg/2 ml versus peak area.

For the internal standard method, use carbon disulfide containing a predetermined amount of the internal standard. The internal standard concentration used was approximately 40% of the concentration at the OSHA standard. The analyte concentration in mg per 2.0 ml is plotted versus the area ratio of the analyte to that of the internal standard.

5. CALCULATIONS

5.1 Read the weight, in mg, corresponding to each peak area from the standard curve. No volume corrections are needed, if the standard curve is based on mg per 2.0 ml carbon disulfide and the volume of sample injected is identical to the volume of the standards injected.

See Method 1a.

5.2 Add the amounts present in the front and backup tubes for the same sample to determine the total weight in the sample.

6. REFERENCES

6.1 Documentation of NIOSH Validation Tests, National Institute for Occupational Safety and Health, Cincinnati, Ohio DHEW-NIOSH-Publication No. 77-185), 1977. Available from Superintendent of Documents, U.S. Government Printing Office, Washington, D.C., Order No. 017-033-0231-2.

6.2 Backup Data Report for Ethyl Chloride, prepared under NIOSH Contract No. 210-76-0123.

6.3 Final Report, NIOSH Contract HSM-99-71-31, "Personal Sampler Pump for Charcoal Tubes:, 15 September 1972.

METHOD 24

(ETHYLENE DIBROMIDE)

Method Ref:	24 (NIOSH S104)
Range:	110 to 470 mg/m^3
Precision:	$(\overline{CV}_T)$ 0.077
Procedure:	Adsorption on charcoal, desorption with carbon disulfide, GC.

1. APPARATUS

1.1 A calibrated personal sampling pump.

1.2 Charcoal tubes: See Method 1a.

1.3 Gas chromatograph equipped with a flame ionization detector.

1.4 Column (10 ft x 1/8 in stainless steel) packed with 10% FFAP on 80/100 Chromosorb W-AW.

1.5 An electronic integrator or some other suitable method for determining peak areas.

1.6 Two millilitre glass sample containers with glass stoppers or Teflon-lined caps. If an automatic sample injector is used, the sample injector vials can be used.

1.7 Microlitre syringes: 10 µl, and other convenient sizes for making standards.

1.8 Pipets: 1.0 ml delivery type.

1.9 Volumetric flasks: 10 ml or convenient sizes for making standard solutions.

2. REAGENTS

2.1 Eluent: Carbon disulfide (chromatographic grade).

2.2 Ethylene dibromide (reagent grade).

2.3 Internal Standard: n-Pentadecane (99+%) or other suitable standard.

2.4 n-Heptane (reagent grade).

2.5 Purifed nitrogen.

2.6 Prepurified hydrogen.

2.7 Filtered compressed air.

3. PROCEDURE

3.1 Cleaning of Equipment. See Method 1a.

3.2 Calibration of Personal Pumps. See Method 1a.

3.3 Collection of Samples

3.3.1 At the T.W.A. concentration a sample size of 10 litres is recommended. Sample at a flow of 0.2 litres per minute. The flow rate should be known with an accuracy of at least ±5%.

At the celing and peak concentrations, a sample size of 1 litre is recommended. Sample for 5 minutes at a flow of 0.2 litres per minute.

3.4 Analysis of Samples

3.4.1 Preparation of Samples. See Method 1a.

3.4.2 Desorption of Samples. Prior to analysis, 1.0 ml of the eluent is pipetted into each sample container. For the internal standard method a 0.2 percent solution of internal standard in the eluent is used.

3.4.3 GC Conditions. The typical operating conditions for the gas chromatograph are:

1. 30 ml/min (80 psig) nitrogen carrier gas flow.
2. 30 ml/min (50 psig) hydrogen gas flow to detector.
3. 300 ml/min (50 psig) air flow to detector.
4. 170°C injector temperature.
5. 210°C manifold temperature (detector).
6. 130°C column temperature.

3.4.4 Injection. Inject 5.0 - 1 of sample.

4. CALCULATIONS

4.1 Read the weights, in mg, corresponding to each peak area (area ratio in case of the internal standard method) from the standard curve. No volume corrections are needed, if the standard curve is based on mg/ml eluent and the volume of sample injected is identical to the volume of the standards injected.

See Method 1a.

5. REFERENCES

5.1 White, L.D., et al., "A Convenient Optimized Method for the Analysis of Selected Solvent Vapors in the Industrial Atmosphere, "Amer. Ind. Hyg. Assoc. J., 31: 225 (1970).

5.2 "Documentation of NIOSH Validation Test", Contract No. CDC-99-74-45.

5.3 Final Report, NIOSH Contract No. HSM-99-71-31. "Personal Sampler Pump for Charcoal Tubes, 15 September 1972".

METHOD 25

(ETHYLENE OXIDE)

Method Ref:	25 (NIOSH S286)
Range:	41 to 176 mg/m^3
Precision:	$(\overline{CV_T})$ 0.103
Procedure:	Absorption on charcoal, desorption with carbon disulfide, GC.

1. APPARATUS

1.1 A calibrated personal sampling pump.

1.2 Charcoal tubes: The sampling tube series consists of two separate large charcoal tubes. The tubes are glass tubes with both ends flame-sealed, 10 cm long with an 8 mm O.D. and 6 mm I.D. Each tube contains the appropriate amount of 20/40 mesh activated coconut charcoal. The front tube contains 400 mg of charcoal; the backup tube 200 mg.

1.3 Gas chromatograph equipped with a flame ionization detector.

1.4 Column (10 ft x 1/8 in. I.D. or O.D. stainless steel) packed with Porapak QS.

1.5 An electronic integrator or some other suitable method for measuring peak areas.

1.6 Five millilitre sample containers with Teflon-lined screw caps, such as the 5 ml vials distributed by SKC, Inc., Pittsburgh, Pennsylvania.

1.7 Microlitre syringes: 10 micolitre, and other convenient sizes for making standards.

1.8 Pipets: 2.0 ml, graduated or delivery.

1.9 Volumetric flasks: 10 ml or convenient sizes for making standard solutions.

2. REAGENTS

2.1 Chromatographic quality carbon disulfide.

2.2 Ethylene oxide, 99.5%. Availabe as a liquid or a gas.

2.3 Purified nitrogen.

2.4 Prepurified hydrogen.

2.5 Filtered compressed air.

METHOD 25

(ETHYLENE OXIDE)

(cont'd)

3. PROCEDURE

3.1 Cleaning of Equipment. See Method 1a.

3.2 Calibration of Personal Pumps. See Method 1a.

3.3 Collection of Samples. See Method 1a.

3.3.1 A sample size of 5 litres is recommended. Sample at a rate of 0.05 litres per minute. The flow rate should be known with an accuracy of at least ±5%.

3.4 Analysis of Samples

3.4.1 Preparation of Samples. See Method 1a.

3.4.2 Desorption of Samples. Prior to analysis, 2.0 ml of carbon disulfide is pipetted into each sample container. Cap the vials tightly immediately after the addition of carbon disulfide. Desorption should be done for 30 minutes, after occasional shaking.

3.4.3 GC Conditions. The typical operating conditions for the gas chromatograph are:

1. 30 ml/min (60 psig) Nitrogen carrier gas flow.
2. 30 ml/min (25 psig) Hydrogen gas flow to detector.
3. 300 ml/min (60 psig) Air flow to detector.
4. 155°C injector temperature.
5. 200°C manifold temperature (detector).
6. 150°C column temperature.

3.4.4 Injection. A 5 µl aliquot is injected.

4. CALCULATIONS

4.1 Read the weight, in mg, corresponding to each peak area from the standard curve. No volume corrections are needed, if the standard curve is based on mg per 2.0 ml carbon disulfide and the volume of the standards injected. See Method 1a or 1b.

5. REFERENCES

5.1 White, L.D., et al, "A Convenient Optimized Method for the Analysis of Selected Solvent Vapors in the Industrial Atmosphere", Amer. Ind. Hyg. Assoc. J., 31: 225 (1970).

5.2 Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.

5.3 Final Report, NIOSH Contract HSM-99-71-31, "Personal Sampler Pump for Charcoal Tubes", 15 September 1972.

METHOD 26a

(FORMALDEHYDE)

Method Ref:	26a
Range:	Unknown
Precision:	Unknown
Procedure:	Collection on impregnated charcoal, desorption with 0.1% H_2O_2 and analysis by IC.

1. APPARATUS

1.1 Dionex Ion Chromatography, Model 10 or equivalent.

1.2 Calibrated personal sampling pump. See Method 1a.

1.3 Charcoal tubes. See Method 1a.

1.4 Associated laboratory glassware.

2. REAGENTS

2.1 Impregnated charcoal (Barneby-Cheney Co., Columbus, Ohio), No. 580-20).

2.2 Sodium formate (Analytical grade).

3. PROCEDURE

3.1 Cleaning of Equipment. See Method 1a.

3.2 Calibration of Personal Sampling Pumps. See Method 1a.

3.3 Collection of Samples. See Method 1a.

A flow rate of 50 to 200 cc/min and a sample duration of 3 to 5 hours is recommended.

4. ANALYSIS OF SAMPLES

4.1 Preparation of Samples. See Method 1a.

4.2 Desorption of samples. Prior to analysis 15.0 ml of 0.1% H_2O_2 is pipetted into each sample container. The samples are mechanically shaken for one hour, then sonicated for 20 minutes.

4.3 Inject sample through a 0.45 μ membrane filter into an Ion Chromatograph.

4.4 Typical IC Conditions

Eluent: 0.005M $Na_2B_4O_7 . 10H_2O$

Flow Rate: 2.3 ml/min

Pre-Column: 3 x 150 mm Anion

Separator: 3 x 500 mm Anion

Suppressor: 6 x 250 mm Anion

Injection Volume: 100µl

Meter full Scale Setting: 30 MHO/cm

5. REFERENCE

5.1 Kim, W.S., Geraci, C.L., Kuper, R.E. "Sampling and Analysis of Formaldehyde in the Industrial Atmosphere." U.S. Dept. of Health, Education and Welfare NIOSH, Cincinnati, Ohio 45226.

METHOD 26b

(FORMALDEHYDE IN AIR)

Method Ref:	26b (NIOSH S173 or P & CAM 125)
Range:	0.1 ppm to 2.0 ppm
Precision:	±5%
Procedure:	Spectrophotometric

1. APPARATUS

1.1 Sampling Equipment. See Method 20.

1.1.1 An integrating volume meter such as a dry gas or wet test meter.

1.1.2 Thermometer

1.1.3 Manometer

1.1.4 Stopwatch

1.2 Spectrophotometer or Colorimeter. An instrument capable of measuring the absorbance of the color developed solution at 580 nm.

1.3 Laboratory glassware

2. REAGENTS

2.1 Chromotrophic Acid Reagent. Dissolve 0.10 g of 4,5-dihydroxy-2, 7-naphthalenedisulfonic acid disodium salt (Eastman Kodak Company, Rochester, New York, Cat. No. P230) in water and dilute to 10 ml. Filter if necessary and store in a brown bottle. Make up fresh weekly.

2.2 Concentrated sulfuric acid.

2.3 Formaldehyde Standard Solution"A" (1 mg/ml). Dilute 2.7 ml of 37 percent formalin solution to 1 litre with distilled water. This solution must be standardized as described in Section 4.1. The solution is stable for at least a 3-month period. Alternatively sodim formaldehyde bisulfite (Eastman Kodak Company, Cat. No. P6450) can be used as a primary standard (Reference 11.4). Dissolve 4.4703 g in distilled water and dilute to 1 litre.

2.4 Formaldehyde Standard Solution "B" (10 µg/ml). Dilute 1 ml of standard solution "A" to 100 ml with distilled water. Make up fresh daily.

2.5 Iodine, 0.1 N (approximate). Dissolve 25 g of potassium iodide in about 25 ml of water, add 12.7 g of iodine and dilute to 1 litre.

2.6 Iodine, 0.01 N. Dilute 100 ml of the 0.1 N iodine solution to 1 litre. Standardize against sodium thiosulfate.

2.7 Starch Solution, 1 per cent. Make a paste of 1 g of soluble starch and 2 ml of water and slowly add the paste to 100 ml of boiling water. Cool, add several ml of chloroform as a preservative and store in a stoppered bottle. Discard when a mold growth is noticeable.

2.8 Sodium Carbonate Buffer Solution. Dissolve 80 g of anhydrous sodium carbonate in about 500 ml of water. Slowly add 20 ml of glacial acetic acid and dilute to 1 litre.

2.9 Sodium Bisulfite, 1 percent. Dissolve 1 g of sodium bisulfite in 100 ml of water. It is best to prepare a fresh solution weekly.

3. PROCEDURE

3.1 Cleaning of Equipment. Care must be exercised to ensure the absence of probable contaminants like organic materials that can be charred by concentrated sulfuric acid. Soaking glassware for one hour in a 1:1 mixture of nitric and sulfuric acids, followed by thorough rinsing with double-deionized water will remove all possible organic contaminants.

3.2 Collection of Samples

3.2.1 Pour 20 ml of absorbing solution (distilled water) into each graduated midget impinger.

3.2.2 Connect two impingers in series to the vacuum pump (via the absorption tube) and the prefilter assembly (if needed) with short pieces of flexible tubing. The minimum amount of tubing necessary to make the joint between the prefilter and impingers should be used. The air being sampled should not be passed through any other tubing or other equipment before entering the impingers.

3.2.3 It has been recommended that two impingers must be used in series because under conditions of sampling, the collection efficiency of only one impinger is approximately 80 per cent. With two impingers in series the total collection efficiency is approximately 95 per cent. The contents of each impinger should be analyzed separately.

3.2.4 Turn on pump to begin sample collection. Care should be taken to measure the flow rate, time and/or volume as accurately as possible. The sample should be taken at a flow rate of 1.0 L/min for one hour. These conditions give a total of 60 litres of air that is drawn through the system. However, a shorter sampling time can be used providing enough formaldehyde is collected to be above the lower limit of sensitivity of the method.

3.2.5 After sampling, the impinger stem can be removed and cleaned. Tap the stem gently against the inside wall of the impinger bottle to recover as much of the sampling solution as possible. Wash the stem with a small amount (1-2 ml) of unused absorbing solution and add the wash to the impinger. Then the impinger is sealed with a hard, non-reactive stopper (preferably Teflon). Do not seal with rubber.

3.3 Analysis

3.3.1 Transfer the sample from each impinger to either a 25 ml or 50 ml graduate cylinder. Note the volume of each solution.

3.3.2 Pipet a 4 ml aliquot from each of the sampling solutions into glass stoppered test tubes. A blank containing 4 ml of distilled water must also be run. If the formaldehyde content of the aliquot exceeds the limit of the method, a smaller aliquot diluted to 4 ml with distilled water is used.

3.3.3 Add 0.1 ml of 1 per cent chromotrophic acid reagent to the solution and mix.

3.3.4 To the solution pipette slowly and cautiously 6 ml of concentrated sulfuric acid. The solution becomes extremely hot during the addition of the sulfuric acid. If the acid is not added slowly some loss of sample could occur due to spattering.

3.3.5 Allow to cool to room temperature. Read at 580 nm in a suitable spectrophotometer using a 1 cm cell. No change in abosrbance was noted over a 3 hour period after color development. Determine the formaldehyde content of the sampling solution from a curve previously prepared from standard formaldehyde solutions.

3.3.6 During the analysis procedure, it is good practice to group together the two impingers from each sampling series and label them as "A" and "B". The formaldehyde content calculated in "A" is added to that calculated in "B" to give the total amount in the sampled atmosphere by the impingers in series.

4. CALIBRATION AND STANDARDS

4.1 Standardization of Formaldehyde Solution

4.1.1 Pipette 1 ml of formaldehyde standard solution "A" into an iodine flask. Into another flask pipette 1 ml of distilled water. This solution serves as the blank.

4.1.2 Add 10 ml of 1 per cent sodium bisulfite and 1 ml of 1 per cent starch solution.

4.1.3 Titrate with 0.1 N iodine to a dark blue color.

4.1.4 Destroy the excess iodine with 0.05 N sodium thiosulfate.

4.1.5 Add 0.01 N iodine until a faint blue end point is reached.

4.1.6 The excess inorganic bisulfite is now completely oxidized to sulfate, and the solution is ready for the assay of the formaldehyde bisulfite addition product.

4.1.7 Chill the flask in an ice bath and add 25 ml of chilled sodium carbonate buffer. Titrate the liberated sulfite with 0.01 N iodine, using a microburette, to a faint blue end point. The amount of iodine added in this step must be accurately measured and recorded.

4.1.8 One ml of 0.0100 N iodine is equivalent to 0.15 mg of formaldehyde. Therefore, since 1 ml of formaldehyde standard solution was titrated, the ml of 0.01 N iodine used in the final titration multiplied by the factor, 0.15, gives the formaldehyde concentration of the standard solution in mg/ml.

4.1.9 The factor, 0.15, must be adjusted or determined accordingly on the basis of the exact normality of the iodine solution.

4.2 Preparation of Standard Curve

4.2.1 Pipet 0, 0.1, 0.3, 0.5, 0.7, 1.0, and 2.0 ml of standard solution "B" into glass stoppered test tubes.

4.2.2 Dilute each standard to 4 ml with distilled water.

4.2.3 Develop the color as describe in the analysis procedure (Section 3.3).

4.2.4 Plot absorbance against micrograms of formaldehyde in the color developed solution. Note that the microgram concentration of the formaldehyde is determined based on the standardization value of solution A.

5. CALCULATIONS

5.1 Convert the volume of air sampled (V) to the volume of air at standard conditions (V_s) of 760 mm of mercury and 25°C, using the correction formula:

$$V_s = V \times \frac{P}{760} \times \frac{298}{(T + 273)}$$

Where:

V_s = volume of air in litres at standard conditions

V = volume of air sampled in litres

P = barometric pressure in mm of mercury

T = temperature of sample air, °C

5.2 Determine the total concentration (C_t) of formaldehyde present in the two sample impingers in series, A and B.

C_t = total µg of formaldehyde in the sample.

C_A and C_B = respective formaldehyde concentration in µg of the sample aliquots taken from impingers A and B as determined from the calibration curve

F_A and F_B = respective aliquot factor; $\frac{\text{sampling soln.vol. in ml}}{\text{ml aliquot used}}$

5.3 The concentration of formaldehyde in the sampled atmosphere may be calculated by using the following equation, assuming standard conditions are taken as 760 mm of mercury and 25°C:

$$\text{ppm (volume)} = \frac{C_t \times 24.47}{V_s \times \text{M.W.}}$$

Where:

V_s = litres of air sampled at standard conditions

M.W. = molecular weight of formaldehyde (30.03)

24.47 = μ of formaldehyde gas in microlitres per micromole at 760 mm Hg and 25°C.

6. REFERENCES

6.1 Altshuller, A.P., Leng, L.J., and Wartburg, A.F., "Source and Atmospheric Analyses for Formaldehyde by Chromotrophic Acid Procedure", Int. J. Air Wat. Poll., 6, 381 (1962).

6.2 Eegriwe, E., "Reaktionen and Reagenzien zum Nachweis Organischer Verbindungen IV", Z Anal. Chem.. 110, 22 (1937).

6.3 Feigl, F., Spot Tests in Organic Analysis, Seventh Ed., American Elsevier Publishing Company, New York, 434, (1966).

6.4 Feldstein, M., (Bay Area Air Pollution Control District) Personal Communication, March 1968.

6.5 MacDonald, W.E., "Formaldehyde in Air - A Specific Field Test," Amer. Ind. Hyg. Assoc. Quarterly, 15, 217 (1954).

6.6 Sleva, S.F., "Determination of Formaldehyde: Chromotropic Acid Method. Selected Methods for the Measurement of Air Pollutants", Public Health Service Publication No. 999-AP-11, H-1, 1965.

6.7 Treadwell and Hall, Analytical Chemistry, Vol. II, Ninth English Edition. John Wiley & Sons, Inc., New York, p. 590, 1951.

6.8 Treadwell and Hall, Analytical Chemistry, Vol. II, Ninth English Edition. John Wiley & Sons, Inc., New York, p. 588, 1951.

METHOD 27

(FORMIC ACID)

Method Ref:	27 (P & CAM 232) (NIOSH S173)
Range:	3.8 to 75 mg/m^3 in a 10 litre sample of air
Precision:	($\overline{CV}_T$) 0.11 (analytical) over the above range
Procedure:	Impinger collection; gas chromatography

1. APPARATUS

1.1 A gas chromatograph equipped with dual flame ionization detectors.

1.2 A stainless steel column (20 ft x 0.125 in) packed with 10% Carbowax 20 M on 80/100 mesh Chromosorb W, or an equivalent column.

1.3 Hamilton gas syringe, 1 ml, or equivalent.

1.4 Reaction vials, 10 ml.

1.5 Teflon-coated septums with tear-away seals for the reaction vials.

1.6 Volumetric pipettes, 2 ml; Eppendorf pipettes, 5, 10, 25, 50, and 100 µl.

1.7 Midget impinger, 15 ml.

1.8 A properly calibrated personal sampling pump capable of sampling at a flow rate of 2.5 l/min for periods of up to 40 min. The pump should be calibrated with a midget impinger containing 15 ml of the absorbing solution in the sampling train. A dry or wet test meter or a glass rotameter that will measure the appropriate flow rate within 5% may be used for the calibration.

1.9 Constant temperature water bath capable of maintaining 55°C.

2. REAGENTS

2.1 Absorbing solution, 0.1N NaOH, dissolve 40 g of sodium hydroxide pellets, ACS reagent grade, in 500 ml distilled water, then make up to 1.0 litre.

2.2 Absolute ethanol (anhydrous), U.V. spectrophotometric grade.

2.3 Sulfuric acid, concentrated, ACS reagent grade.

2.4 Ethyl formate, 99%.

2.5 Derivatizing Solution. To a 100 ml graduated cylinder add 70 ml of absolute ethanol. To the ethanol slowly add 20 ml of concentrated sulfuric acid. Allow the solution to cool to room temperature. Add ethanol until the volume is 100 ml and mix.

2.6 Sodium Formate Solution. In a 100 ml volumetric flask, dissolve 0.1478 g of sodium formate, ACS reagent grade, in 0.1 N NaOH and fill to the mark with 0.1 N NaOH. This solution is equivalent to a formic acid concentration of 1000 µg/ml.

2.7 Helium, Bureau of Mines Grade A, or equivalent.

2.8 Prepurified hydrogen.

2.9 Filtered compressed air.

3. PROCEDURE

3.1 Cleaning of Equipment. Wash all glassware in detergent solution and rinse with tap water. Soak the glassware in chromic acid cleaning solution (saturated solution of sodium dichromate in concentrated sulfuric acid) and rinse with tap water and distilled water.

3.2 Collection of Samples

3.2.1 Cleaning of Equipment. Wash all glassware in detergent solution and rinse with tap water. soak the glassware in chromic acid solution (saturated solution of sodium dichromate in concentrated sulfuric acid) and rinse with tap water and distilled water.

3.2.2 Turn on the pump to begin sample collection. Measure the flow rate and time, or volume, as accurately as possible and record the temperature and pressure of the atmosphere being sampled. Sample at a flow rate of 2.5 l/min. Collect a sample of 45 to 100 litres. A sample of 100 litres of air will allow measurement of at least 0.9 mg/m^3, one tenth the OSHA standard. See Method 20.

3.3 Analysis of Samples

3.3.1 Withdraw a 2 ml aliquot from the impinger and place it in a 10 ml reaction vial.

3.3.2 Add 2 ml of derivatizing solution to the vial and seal it immediately with a Teflon-coated septum.

3.3.3 Place the sealed vial in a constant temperature water bath at 55°C for 2 hrs.

3.3.4 After 2 hrs., pierce the septum with the needle of the gas syringe.

3.3.5 Flush the syringe three times with the headspace gas.

3.3.6 Inject 1 ml of the headspace gas into the gas chromatograph. The operating conditions for the gas chromatographic analysis are as follows:

1. Helium carrier gas flow rate, 30 ml/min.
2. Hydrogen gas flow rate to the detector, 65 ml/min.
3. Air flow rate to the detector, 500 ml/min.
4. Injector temperature, 150°C.
5. Detector temperature, 150°C.
6. Column temperature, 70°C.

3.3.7 Measure the height of the ethyl formate peak. The retention time of ethyl formate is determined by injecting ethyl formate vapor into the gas chromatograph before the sample is injected.

4. CALIBRATION AND STANDARDS

4.1 To 2 ml of distilled water in each of five 10 ml reaction vials add the amounts of sodium formate solution specified in the following table to prepare the five standards necessary for the calibration curve.

Vial No.	Volume of sodium formate solution (ml)	Equivalent amount of formic acid per vial (µg)
1	0.100	100
2	0.050	50
3	0.025	25
4	0.010	10
5	0.005	5

Standards of higher concentration may also be prepared.

4.2 Analyze the standards by the procedure described in Sections 3.3.2 to 3.3.7. Plot the height of the ethyl formate peak as a function of the equivalent amount (in µg) of formic acid in each vial.

5. CALCULATIONS

5.1 From the standard curve, read the weight (in µg) of formic acid corresponding the the peak height for the headspace sample. If the blank impinger solution produces a peak with the same GC retention time as the ethyl formate peak, subtract the calculated amount of formic acid from the sample value. To calculate the total amount of formic acid collected in the sample, use the following equation:

$$W = \frac{W_c \times I}{A}$$

Where:

W = amount of formic acid (µg) collected in the impinger.

W_c = amount of formic acid (µg) read from the calibration curve and corrected for the blank.

I = volume of the impinger sample (15 ml).

A = volume of the aliquot taken (2 ml).

5.2 The concentration of formic acid in air may be expressed in mg/m^3:

$$mg/m^3 = \frac{W\ (\mu g)}{V_S\ (l)}$$

where: V_S = volume of air sampled.

6. References

6.1 Mraz, M., and Sedwec, V., "Determination of Toxic Substances and Their Metabolites in Biological Fluids by Gas Chromatography. VIII. Formic Acid in Urine", Collect. Czech. Chem. Commun., 38, 3426 (1973).

6.2 Smallwood, A.W., "Analysis of Formic Acid in Air Samples", presented at American Industrial Hygiene Conference, Atlanta, Georgia, May 1976.

METHOD 28

(FURFURYL ALCOHOL)

Method Ref:	28(NIOSH S365)
Range:	120 to 470 mg/m^3
Precision:	($\overline{CV}_T$) 0.072
Procedure:	Adsorption on Porapak Q, desorption with acetone, GC

1. APPARATUS

1.1 Personal sampling pump.

1.2 Porapak Q Tubes: Glass tube with both ends unsealed, 8.5 cm long with a 6 mm o.d. and a 4 mm i.d., containing two sections of 50/80 mesh Porapak Q separated by a 2 mm portion of urethane foam. The adsorbing section of the tube contains 150 mg of Porapak Q and the backup section contains 75 mg.

Sorbent Washing Procedure: Prior to usage, Porapak Q is washed and dried to reduce or eliminate the effects of reacted monomers, solvents and manufacturer's batch to batch differences in glass filters fitted to a large vacuum flask. Reagent grade acetone, equal to twice the volume of Porapak Q is added to the sorbent and mixed and a vacuum is applied. Repeat the operation of wash-mix-vacuum six times. The sorbent is then transferred to an evaporating dish and dried in a vacuum oven at 120°C under 25 inches mercury vacuum for four hours.

1.3 Gas chromatograph equipped with a flame ionization detector.

1.4 Column (3 ft. long x 1/8 inch o.d. stainless steel) packed with 50/80 mesh Porapak Q.

1.5 An electronic integrator or some other suitable method of determining peak areas.

1.6 Sample Containers: 2.0 ml glass sample containers with glass stoppers or Polyseal caps or equivalent.

1.7 Microliter Syringes: 10 µl and other convenient sizes for preparing standards.

1.8 Pipets: Delivery type, 1.0 ml and other convenient sizes.

1.9 Volumetric Flasks: 10 ml and other convenient sizes for preparing standard solutions.

1.10 Stopwatch

1.11 Manometer

2. REAGENTS

2.1 Acetone, reagent grade.

2.2 Furfuryl alcohol.

2.3 Benzene, chromatographic quality.

2.4 Nitrogen, purified.

2.5 Hydrogen prepurified.

2.6 Air, filtered, compressed.

3. PROCEDURE

3.1 Cleaning of Equipment. See Method 1a.

3.2 Calibration of sampling pumps. See Method 1a.

3.3 Collection of samples.

3.3.1 A Sample size of 6 l is recommended. Sample at a flow rate between 0.01 and 0.05 l/min. Do not sample at a flow rate less than 0.010 l/min. Record the sampling time, flow rate and type of sampling pump used. See Method 1a.

3.4 Analysis of samples:

3.4.1 Preparation of samples. See Method 1a.

3.4.2 Desorption of samples. Prior to analysis, 1.0 ml of acetone is pipetted into each sample container. Cap and shake the sample vigorously. Desorption is complete in 15 minutes. Analyses should be completed within one day after the furfuryl alcohol is desorbed.

3.4.3 GC Conditions. The typical operating conditions for the gas chromatograph are:

1. 50 ml/min (60 psig) nitrogen carrier gas flow
2. 65 ml/min (24 psig) hydrogen gas flow to detector
3. 500 ml/min (50 psig) air flow to detector
4. 225°C injector manifold temperature
5. 225°C detector manifold temperature
6. 200°C column temperature

3.4.4 Injection. A 5 µl aliquot is injected.

4. CALCULATIONS

4.1 Read the weight, in mg, corresponding to each peak area from the standard curve. No volume corrections are needed if the standard curve is based on mg/1.0 ml acetone and the volume of sample injected is identical to the volume of the standards injected. See Method 1a or 1b.

5. REFERENCES

5.1 Documentation of NIOSH Validation Tests, NIOSH Contract CDC-99-74-45.

5.2 Backup Data Report for Furfuryl Alcohol, prepared under NIOSH Contract No. 210-76-0123.

5.3 Final Report, NIOSH Contract HSM-99-71-31, "Personal Sampler Pump for Charcoal Tubes", 15 September 1972.

METHOD 29

(HYDROGEN CHLORIDE)

Method Ref:	29(NIOSH S246)
Range:	3.5 to 14 mg/m^3
Precision:	$(\overline{CV}_T)$ 0.064
Procedure:	Bubbler collection in 0.5 M sodium acetate, ion specific electrode

1. APPARATUS

1.1 Sampling Equipment. See Method 20.

1.1.1 An integrating volume meter such as a dry gas or wet test meter.

1.1.2 Thermometer

1.1.3 Manometer

1.1.4 Stopwatch

1.2 Pipets: 1, 2, 3, 5 and 10 ml

1.3 Orion Model 94-17A chloride specific ion electrode, or equivalent.

1.4 Reference electrode. Orion 90-02 double junction, or equivalent.

1.5 Expanded scale millivolt pH meter, capable of measuring to within 0.5 millivolt.

1.6 Polyethylene beakers, 50 ml capacity. Premark the beakers by pipetting 25 ml of distilled water into each beaker and mark the liquid level. Pregraduated polyethylene beakers may be used. However, they should be checked as described above. Discard the water and dry the beakers.

1.7 Magnetic stirrer and stirring bars for 50 ml beakers.

1.8 Polyethylene containers. These containers should be used to store diluted sodium chloride standards and also for shipping of air samples.

1.9 100 ml volumetric flasks.

2. REAGENTS

All chemicals must ACS reagent grade or equivalent.

2.1 Double distilled water.

2.2 Collection medium: 0.5 M sodium acetate solution. Dissolve 82 g of sodium acetate in doubly distilled water and dilute to 2 l.

2.3 Sodium chloride, for preparation of standards.

2.4 Standard chloride solution.

2.4.1 Dissolve 0.584 g of sodium chloride in double distilled water and dilute to 1 litre for 10^{-2} M ($C\ell^-$) or 354 µg $C\ell^-$/ml. Adjust the pH to 5 with glacial acetic acid. This solution is stable for about two months. Appropriate dilute standards may be prepared from the stock solution.

3. PROCEDURE

3.1 Cleaning of equipment. See Method 1a.

3.2 See Method 20.

3.3 Collection and samples.

3.3.1 Pour 10 ml of the collection medium (Section 2.2) into the midget bubbler, using a graduated cylinder to measure the volume. See Method 21.

3.4 Analysis of samples.

3.4.1 The sample in each polyethylene container is analyzed separately.

3.4.2 Quantitatively transfer the contents of each polyethylene container to a 50 ml polyethylene beaker which has been premarked at 25 ml. Rinse the polyethylene container with 2 to 3 ml of distilled water and add rinse to the beaker. Adjust the pH to 5 with acetic acid and check the pH with pH paper. Dilute each sample to 25 ml with distilled water and stir the samples with a magnetic stirrer.

3.4.3 Lower the chloride ion specific electrode and reference electrode into the stirred solution and record the resulting millivolt reading (to the nearest 0.5 mV) after it has stabilized (drift less that 0.5 mV/min.).

4. CALCULATIONS

4.1 Read the weight in µg corresponding to each millivolt reading from the standard curve. No volume corrections are needed, if the standard curve is based on µg/25 ml volume and the volume of samples is identical to the volume of the standards. See Method 1a or b for computing the results.

5. REFERENCES

5.1 "Analytical Method for Chloride in Air", Health Laboratory Science, Vol. 12, No. 3, (July 1975), 253-258.

5.2 Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.

METHOD 30

(FLUORIDE AND HYDROGEN FLUORIDE)

Method Ref:	30 (NIOSH S176)
Range:	0.05 to 475 mg/m^3 fluoride
Precision:	6.5% RSD for 100 µg HF
Procedure:	Collection via impinger, ion specific electrode

1. APPARATUS

1.1 Sampling Equipment. The sampling unit for the impinger collection method consits of the following components:

1.1.1 A prefilter unit, which consits of a cassette filter holder with Teflon filter, may be used to remove particulates and allow for gaseous flourides only.

1.1.2 A midget impinger containing the absorbing solution or reagent.

1.1.3 A pump suitable for delivering desired flow rates, The sampling pump is protected from splashover or water condensation by an adsorption tube loosely packed with a plug of glass wool and inserted between the exit arm of the impinger and the pump.

1.1.4 An integrating volume meter such as a dry gas or wet test meter.

1.1.5 Thermometer

1.1.6 Manometer

1.1.7 Stopwatch

1.2 Fluoride Specific Ion Electrode, or equivalent.

1.3 Reference Electrode, or equivalent calomel or silver/silver chloride electrode.

1.4 Expanded scale Millivolt-pH Meter, capable of measuring to within 0.5 millivolt.

1.5 Polyethylene Beakers, 50 ml capacity.

1.6 Laboratory glassware.

1.7 Magnetic stirrer and stirring bars for 50 ml beakers.

2. REAGENTS

All chemicals must be ACS reagent grade or equivalent. Polyethylene beakers and bottles should be used for holding and storing all fluoride-containing solution.

2.1 Double distilled water.

2.2 Glacial acetic acid.

2.3 Absorbing Solution: 0.1 M Sodium Hydroxide Solution. Dissolve 4 g sodium hydroxide pellets in 1 litre distilled water.

2.4 Sodium Hydroxide, 3.5 M Solution. Dissolve 28 g sodium hydroxide pellets in sufficient distilled water to give 200 ml of solution.

2.5 Sodium chloride.

2.6 Cyclohexane diamine tetraacetic acid monohydrate (CDTA).

2.7 Total Ionic Strength Activity Buffer (TISAB). Place 650 ml of double distilled water in a 1 litre beaker. Add 57 ml of glacial acetic acid, 58 g of sodium chloride and 30 g of CDTA. Stir the solution for 15 minutes. The CDTA may not go completely into solution until the sample volume approaches one litre during the following steps. Place the beaker in a water bath (for cooling) and slowly add 3.5 M sodium hydroxide with stirring until the pH is 5.0 $\pm$0.1. Cool to room temperature and pour into a 1 litre volumetric flask and add double distilled water to the mark.

2.8 Sodium Fluoride, for preparation of standards.

2.9 Standard fluoride Solution. The stock solution (0.1 M F^-) is stable for two months. The dilution standards should be prepared every two weeks.

2.9.1 Dissolve 4.2 g of sodium fluoride in double distilled water and dilute to 1 litre. This solution contains 10^{-1} M F^- (1900 µg F^-/ml).

2.9.2 Prepare solutions containing 190, 19, 1.9 and 0.19 µgF^-/ml by diluting appropriate stock solutions.

3. PROCEDURE

3.1 Cleaning of Equipment. All glassware and plasticware are washed in detergent solution, rinsed in tap water, and then rinsed with double distilled water.

3.2 Collection and Shipping of Samples

3.2.1 Pour 10 ml of absorbing solution into the midget impinger, using a graduated cylinder to measure the volume.

3.2.2 Connect the impinger (via the adsorption tube) to the vacuum pump and the prefilter assembly (if needed) with a short piece of flexible tubing. The minimum amount of tubing necessary to make the joint between the prefilter and impinger should be used. The air being sampled should not be passed through any other tubing or other equipment before entering the impinger.

3.2.3 Turn on pump to begin sample collection. Care should be taken to measure the flow rate, time, and/or volume as accurately as possible. The sample should be taken at a flow rate of 2.5 L/min. A sample size of not more than 200 litres and no less than 40 litres should be collected. The minimum volume of air sampled will allow the measurement of at least 1/10 times the TLV, 0.2 mg/m^3 (760 mm Hg, 25°C).

3.2.4 Record the temperature and pressure of the atmosphere being sampled. If the pressure reading is not available, record the elevation. Also report the type of sampling pump used.

3.2.5 After sampling, the impinger stem can be removed and cleaned. Tap the stem gently against the inside wall of the impinger bottle to recover as much of the sampling solution as possible. Wash the stem with a small amount (1.2 ml) of unused absorbing solution and add the wash to the impinger. Then the impinger is sealed with a hard, non-reactive stopper (preferably Teflon). Do not seal with rubber. The stoppers on the impingers should be tightly sealed to prevent leakage during shipping. If it is preferred to ship the impingers with the stems in, the outlets of the stem should be sealed with Parafilm or other non-rubber covers, and the ground glass joints should be sealed (i.e. taped) to secure the top tightly.

3.2.6 Care should be taken to minimize spillage or loss by evaporation at all times. Refrigerate samples if analysis cannot be done within a day.

3.2.7 A "blank" impinger should be handled as the other samples (fill, seal, and transport) except that no air is sampled through this impinger.

3.3 Analysis of Samples

3.3.1 The sample is transferred from the impinger to a 25 ml graduated cylinder. Use 2 or 3 ml of double distilled water to rinse the impinger and add the rinse to the graduated cylinder. Add 10 ml of TISAB to the graduate cylinder and sufficient double distilled water to bring the volume to 25 ml. Stir or shake the solution to promote complete mixing. Pour the contents of the graduated cylinder into a 50 ml plastic beaker. Any drops remaining in the graduated cylinder can be disregarded since this will not affect the results.

3.3.2 Place the beaker on a stirrer and lower the fluoride selective electrode and the reference electrode into the stirred solution. After the electrodes have stabilized for 10 minutes, record the meter reading to the nearest 0.1 millivolt.

4. CALIBRATION AND STANDARDS

Prepare a series of fluoride standard solutions by pipetting 10 ml of each fluoride standard into clear polyethylene beakers. Then pipet 10 ml of TISAB and 5 ml of double distilled water into each of the beakers. Insert the fluoride ion electrode and the reference electrode into each of the stirred calibration solutions starting with the most dilute solution and record the resulting millivolt reading to the nearest 0.5 millivolt. Plot the millivolt reading vs. the fluoride ion concentration of the standards on semi-log paper. Use the concentration of the standards before dilution for plotting, not the dilute concentration. The fluoride ion concentration in µg ml is plotted on the log axis.

5. CALCULATIONS

5.1 The concentration (µg/ml) of fluoride in the sample solution is obtained from the calibration curve.

5.2 Total µg F^- in the sample = sample concentration (µg/ml) x 10.0 ml.

5.3 Convert the volume of air sampled to standard conditions of 25°C and 760 mm Hg.

$$V_s = V \times \frac{P}{760} \times \frac{298}{T + 273}$$

5.4 The total µg F^- is divided by the volume, in litres, of air sampled to obtain concentration in µg F^-/litre or mg F^-/m^3.

$$\text{mg } F^-/m^3 = \mu\text{g } F^-/\text{litre}$$

$$\text{mg } F^-/m^3 = \frac{\text{total } \mu\text{g } F^-}{V_N} \qquad \text{(Section 10.3)}$$

Where:

V_s = volume of air in litres at 25°C and 760 mm Hg

V = volume of air in litres as measured

P = barometric pressure in mm Hg

T = temperature of air in degrees centigrade

5.5 The concentration can also be expressed in ppm, defined as 1 of component per litre of air.

$$\text{ppm } F^- = \mu\text{l } F^-/V_s = \frac{24.45}{MW} \times \mu\text{g } F^-/V_s$$

$$= 1.29 \ \mu\text{g } F^-/V_s$$

Where:

24.45 = molar volume at 25°C and 760 mm Hg

MW = 19, weight of fluoride ion,
(i.e. 19 µg F^- = 24.45 µl at 25°C, 760 mm Hg)

5.6 To calculate the concentration of hydrogen fluoride as mg HF/m^3, multiply concentration of F^- (from 10.4) by 1.05. The concentration of hydrogen fluoride as µl/l or ppm is identical to the F^- concentration as µl F^-/l (from Section 10.5).

6. REFERENCES

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METHOD 31a

(HYDROGEN PEROXIDE)

Method Ref:	31a
Range:	0 to 6 µg/ml
Precision:	Unknown
Procedure:	Collection on coarse fritted bubbler containing aqueous $TiSO_4/(NH_4)_2SO_4/H_2SO_4$ solution. Absorbance at 450 nm measured after reaction with quinolinol at pH 4.2.

1. APPARATUS

   1.1 Spectrophotometer set at 450 nm.

   1.2 Coarse fritted bubbler(s)

   1.3 Personal sampling pump(s)

   1.4 Flow meter to calibrate pump(s)

   1.5 Sintered glass funnel

   1.6 pH meter

2. REAGENTS

   2.1 Chloroform

   2.2 Concentrated H_2SO_4

   2.3 $TiSO_4$

   2.4 $(NH_4)_2SO_4$

   2.5 Distilled and dionized water

   2.6 Hydrogen peroxide standard, 600 µg H_2O_2/ml

   2.7 Potassium iodide

   2.8 Starch solution

   2.9 Sodium acetate buffer, 5 per cent

   2.10 8-Quinolinol

   2.11 Anhydrous sodium sulphate

3. PROCEDURE

3.1 Sample Collection

3.1.1 Gently heat 4.5 gm $TiSO_4$ and 20 gm $(NH_4)_2SO_4$ in 100 ml of concentrated H_2SO_4 until dissolved. Cool and pour into 350 ml of water. Filter through a sintered glass funnel and dilute to 500 ml. This is the stock reagent.

3.1.2 Dilute the stock solution 50 : 1 to obtain a sampling reagent with approximately 50 µg Ti (IV) per ml. Fill the bubbler with 15 ml of this reagent.

3.1.3 Draw air through the bubbler at a flow rate of 0.5 L.p.m. for 3 hours.

3.1.4 Seal the bubbler for transport or transfer to a glass stoppered vial for transport.

3.1.5 One blank should be submitted for every 10 samples.

3.2 Analysis:

3.2.1 Adjust the pH of the bubbler solution to 4.2 $\pm$ 0.2 with the 5 per cent sodium acetate buffer.

3.2.2 Transfer the buffered solution to a separatory funnel and shake for 5 minutes with 10 ml of 0.1 per cent 8-quinolinol in chloroform.

3.2.3 Isolate the chloroform layer and dry over anhydrous sodium sulphate.

3.2.4 Measure the absorbance at 450 nm.

3.2.5 The coloured complex should be protected from the light prior to analysis as it will fade.

4. CALIBRATION STANDARDS

4.1 At least four standards should be prepared from hydrogen peroxide stock solution. The stock solution should be standardized against potassium iodide.

4.2 The four standards are analyzed with aliquots of the Ti (IV) reagent as described above.

4.3 The absorbance at 450 nm is plotted versus concentration and the sample concentrations may be read directly from the curve.

METHOD 31b

(HYDROGEN PEROXIDE)

Method Ref:	31b
Range:	1 ppb to 1 ppm (liquid phase)
Precision:	At 20 ppb the standard deviation is 4 per cent
Procedure:	Collection with impinger, chemiluminescent reaction with 5-amino-2,3-dihydro-1,4-phthalazinadione (luminol) in the presence of Cu^{2+} catalyst. Technician autoanalyzer with photomultiplier tube sensitive to the 450 nm region.

1. APPARATUS

1.1 Technician Auto Analyzer Type # peristaltic pump

1.2 Flow-rated pump tubing : 0.32 ml/min, 0.40 ml/min, 0.60 ml/min

1.3 Altex 201-06 slide sample injection valve with a 1.0 ml sample loop

1.4 Flat spiral reaction cell of 4 mm O.D. glass tubing

1.5 Blue sensitive, high gain, RCA-4507 photomultiplier tube (PMT)

1.6 Keithly 414 S picoammeter to amplify PMT output

1.7 Strip chart recorder

1.8 Midget impingers

1.9 Personal sampling pumps

1.10 Flow meter to calibrate pumps

1.11 1/16 inch O.D. Teflon tubing

1.12 Associated laboratory and sampling equipment

2. REAGENTS

2.1 Distilled deionized water

2.2 5-amino-2,3-dihydro-1,4-phthalazinedione, monosodium salt

2.3 Copper (II) Nitrate

2.4 1 per cent hydrogen peroxide stock solution

2.5 Standard $KMnO_4$ solution.

2.6 NaOH solution

3. PROCEDURE

3.1 Sampling:

3.1.1 The air is passed through a midget impinger containing 10 ml of water using a sampling pump calibrated for 1 L.p.m. with the impinger in line. The duration of the sample is 20 minutes. A plug of glass wool should be loosely inserted in the tubing between the pump and impinger to protect the pump for splashback.

3.1.2 At the conclusion of sampling the impinger is sealed for transport or the solution is transferred to a glass stoppered glass vial for transport.

3.1.3 The impinger solution should be analyzed within 30 minutes of the conclusion of sampling or refrigerated if longer times will elapse prior to analysis.

3.1.4 One impinger blank should be submitted with every 10 samples.

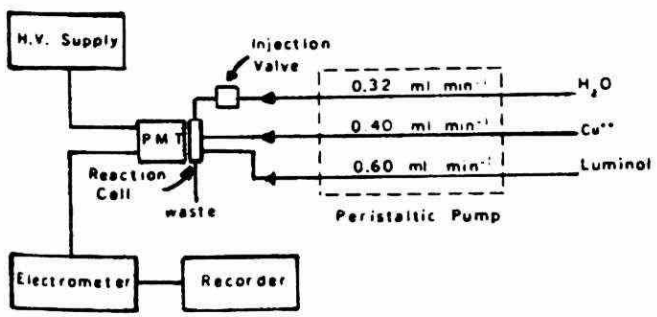
NOTE: The presence of metal ions will cause a strong positive interference. Concentrations of SO_2 exceeding 1 ppm will cause a strong negative interference. Peroxyacetyl nitrate (PAN) may cause some positive interference.

3.2 Analytical Instrument:

3.2.1 The system is assembled as illustrated in Figure 1.

All tubing except the pump tubing is 1/16 in. Teflon.

Figure 1. Analytical System for Measurement of H_2O_2 in Liquid Phase



3.2.2 The Altex injection valve is used to inject samples and standards into the system.

3.2.3 The reaction cell should be positioned with 2 mm of the PMT for optimum light collection.

3.2.4 No optical filtering is employed as there are no known interfering chemiluminescent reactions.

3.3 Sample Analysis:

3.3.1 The pH of the samples is adjusted to 12.8 with NaOH prior to analysis.

3.3.2 The luminol should be prepared with a concentration of 2.4 x 10^{-4} M and the copper (II) nitrate with a concentration of 1.5 x 10^{-5} M.

3.3.3 The blanks and standards are analyzed in the same manner as the samples.

3.3.4 Introduce the sample into the instrument and read the concentration from the calibration curve.

4. CALIBRATION STANDARDS

4.1 The working standards are prepared daily from the stock 1 per cent hydrogen peroxide. This stock solution should be standardized prior to each usage, against standard $KMnO_4$ solution.

4.2 Five standards should be prepared by diluting the stock solution. These should cover the range of concentrations of interest.

4.3 Sample concentrations may be obtained directly from the calibration curve which is prepared by plotting concentration versus peak height.

METHOD 32

(HYDROGEN SULFIDE)

Method Ref:	32 (NIOSH S4)
Range:	8.5 to 63 mg/m^3
Precision:	$(\overline{CV_T})$ 0.121
Procedure:	Absorption - Methylene Blue Spectrophotometric

1. APPARATUS

1.1 Sampling Equipment. The sampling unit for the impinger collection method consists of the following components:

1.1.1 A graduated 25 ml midget impinger with a standard glass-tapered gas delivery tube containing the absorbing solution or reagent. The impinger should be wrapped in aluminum foil to protect the sample from exposure to light.

See Method 20.

1.1.2 Thermometer

1.1.3 Manometer

1.1.4 Stopwatch

1.2 Laboratory glassware

1.3 Colorimeter with red filter or spectrophotometer at 670 nm.

1.4 Matched cells, 1 cm path length.

2. REAGENTS

All reagents must be ACS analytical reagent quality. Distilled water should conform to the ASTM Standards for Referee Reagent Water.

All reagents should be refrigerated when not in use.

2.1 Amine-sulfuric Acid Stock Solution. Add 50 ml concentrated sulfuric acid to 30 ml water and cool. Dissolve 12 g of N,N-dimethyl-p-phenylenediamine dihydrochloride or 10.5 g N,N-dimethyl-p-phenylenediamine oxalate may be used (para-aminodimethylaniline) (redistilled if necessary) in the acid. Do not dilute. The stock solution may be stored indefinitely under refrigeration.

2.2 Amine Test Solution. Dilute 25 ml of the Stock Solution to 1 litre with 1:1 sulfuric acid.

2.3 Ferric Chloride Solution. Dissolve 100 g of ferric chloride, $FeCl_3.6H_2O$ in water and dilute to 100 ml.

2.4 Ethanol, 95%.

2.5 STRactan 10. (Arabinogalactan) Available from Chicago Scientific Inc., 716 W. Irving Park Road, Bansenville, Illinois 60106. Arabinogalactan sold under other brand names may be used.

2.6 Cadmium Sulfate-STRactan Solution. Dissolve 8.6 g of $3CdSO_4.8H_2O$ in approximately 600 ml. of water. Add 20 g STRactan 10 and dilute to 1 litre.

2.7 Sodium Hydroxide Solution. Dissolve 0.6 g sodium hydroxide in approximately 600 ml of water and dilute to 1 litre.

2.8 Cadmium Hydroxide-STRactan Absorbing Solution. This absorbing solution is prepared by pipetting 5 ml of cadium sulfate-STRactan solution (2.6) and 5 ml of sodium hydroxide solution (2.7) directly into the midget impinger and mixing. This solution is stable for 3 to 5 days.

2.9 Stock Sodium Sulfide Standard. Place 35.28 g of $Na_2S.9H_2O$ into a 1 litre volumetric flask and add enough oxygen free distilled water to bring the volume to 1 litre. Store under nitrogen and refrigerate. Standardize with standard iodine and thiosulfate solution in an iodine flask under a nitrogen atmosphere to minimize air oxidation. The approximate concentration of the sulfide solution will be 4700 g sulfide/ml of solution. The exact concentration must be determined by iodine-thiosulfate standardization immediately prior to dilution.

2.10 Working Sodium Sulfide Solution. Dilute 25 ml of stock solution (2.9) with oxygen free water to 250 ml. This solution contains the sulfide equivalent of approximately 500 g/ml of H_2S. Make fresh working sulfide solution daily. The actual concentration of this solution can be determined from the titration results on the stock sodium sulfide standard (2.9).

For the most accurate results in the iodometric determination of sulfide in aqueous solution, the following general procedure is recommended:

1. Replace the oxygen from the flask by flushing with an inert gas such as carbon dioxide or nitrogen.

2. Add an excess of standard iodine, acidify, and back titrate with standard thiosulfate and starch indicator (ref. 11.14).

3. PROCEDURE

3.1 Cleaning of Equipment. All glassware should be thoroughly cleaned. The following procedure is recommended:

3.1.1 Wash with a detergent and tap water solution followed by tap water and distilled water rinses.

3.1.2 Soak in 1:1 or concentrated nitric acid for 30 minutes and then follow with tap, distilled, and double distilled water rinses.

3.2 Collection of Samples:

3.2.1 Prepare 10 ml of absorbing solution as described in Section 2.8 directly in the midget impinger. The addition of 5 ml of 95% ethanol to the absorbing solution just prior to aspiration controls foaming for 2 hours (induced by the presence of STRactan 10). In addition, 1 or 2 Teflon Demister discs may be slipped up over the impinger air inlet tube to a height approximately 1 to 2 in. from the top of the tube. Wrap the impinger with aluminum foil.

See Method 20.

3.2.2 At the ceiling and peak concentrations, a sample size of 2 litres is recommended. Sample for 10 minutes at a flow of 0.20 litres per minute. The flow rate should be known with an accuracy of at least $\pm$ 5%.

3.3 Analysis of Samples:

3.3.1 Remove the impinger top and drain it thoroughly into the impinger bottom. Set aside. Transfer the solution and deposit in the impinger bottom to a 250 ml volumetric flask. Using 50 ml of distilled water rinse the bottom twice with the aid of a clean rubber policeman on a glass stirring rod. Add the rinse solutions to the volumetric flask. With the aid of the rubber policeman wash the outside of the impinger stem with 20 ml of distilled water and add the washings to the flask and drain 20 ml of distilled water and add the washings to the flask and drain 20 ml of distilled water through it into the flask. The total wash water volume should be 90 ml.

3.2.2 Add 15 ml of amine test solution through the impinger inlet tube into the volumetric flask. This is necessary to dissolve the CdS deposited inside the inlet tube. Mix gently to avoid loss of H_2S.

3.3.3 Add 0.5 ml of ferric chloride solution and mix. Bring to volume with distilled water. Allow to stand 20 minutes.

3.3.4 Measure the absorbance of the color at 670 nm in a spectrophotometer or colorimeter set at 100 per cent transmission against the zero reference.

4. CALIBRATION AND STANDARDS

4.1 Aqueous Sulfide

4.1.1 Place 5 ml of each of the absorbing solutions (Sections 2.6 and 2.7) into each of a series of 250 ml volumetric flasks. Add standard sulfide solution equivalent to 0, 20, 40, 80, 120, 160 g of hydrogen sulfide to the different flasks.

4.1.2 Add 90 ml of distilled water.

4.1.3 Add 15 ml of amine-acid test solution to each flask and mix gently.

4.1.4 Add 0.5 ml of ferric chloride solution to each flask. Mix, make up to volume, and allow to stand for 20 minutes.

4.1.5 Determine the absorbance in a spectrophotometer at 670 nm against the sulfide-free reference solution.

4.1.6 Prepare a standard curve of absorbance versus g H_2S.

4.2 Gaseous Sulfide. Cylinders of hydrogen sulfide in dry nitrogen in the range desired are available commercially, and may be used to prepare calibration curves for use at the 10-60 mg/m^3 levels; nitrogen containing hydrogen sulfide in the 450-600 ml/m^3 range can be diluted to the desired concentrations. Analyses of these known concentrations give calibration curves which simulate all of the operational conditions performed during the sampling and chemical procedure. This calibration curve includes the important correction for collection efficiency at various concentrations of hydrogen sulfide.

4.2.1 Prepare or obtain a cylinder of nitrogen containing hydrogen sulfide in the range of 450-600 mg/m^3.

4.2.2 To obtain standard concentrations of hydrogen sulfide, assemble the apparatus consisting of appropriate pressure regulators, needle valves and flow meters for the nitrogen and for a dry air diluent stream. All stainless steel, glass or rubber tubing must be used for the hydrogen sulfide mixture. Flow of hydrogen sulfide in nitrogen is controlled by a needle valve operated in conjunction with a previously calibrated flow meter in the range of 0.2 to 2.0 litres per minute. Diluent dry air from a cylinder is controlled by a similar needle valve-flow meter combination in the range of 1 to 20 litres per minute. The hydrogen sulfide in nitrogen and the diluent air are combined in a mixing chamber at atmospheric pressure, from which they flow through a baffle tube in which mixing takes place into a 1 litre sampling flask which is provided with one or more nipples from which samples can be taken. sampling is done by connecting a midget impinger to the nipple and drawing a known volume of the mixture through the impinger for a measured length of time, using a critical orifice to control flow at a constant known rate.

5. CALCULATIONS

5.1 Gaseous Sulfide

5.1.1 Using the Beers-Law Standard curve of absorbance versus g H_2S determine g H_2S in the sampling impinger corresponding to its absorbance reading at 670 nm.

5.1.2 The concentration of H_2S in the air sampled can be expressed in mg/m^3 which is numerically equal to g/litre.

$$mg/m^3 = g/litre = \frac{g\ H_2S}{\text{Air volume sampled (litre)}}$$

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METHOD 33

(MALEIC ANHYDRIDE)

Method Ref:	33 (P & CAM 302 or NIOSH 302)
Range:	0.50 to 2.14 mg/m^3
Precision:	(RSD) 0.063
Procedure:	Bubbler Collection, HPLC

1. APPARATUS

1.1 Glass midget bubblers with fritted glass stems.

1.2 Personal Sampling Pump.

1.3 Manometer

1.4 Thermometer

1.5 HPLC equipped with a U.V. detector at 254 nm and a sample injection valve with a 50 microlitre sample loop.

1.6 HPLC COLUMN (300 mm x 3 mm I.D. stainless steel) packed with μ-Bondpak C-18*, or equivalent.

1.7 An electronic integrator or some other suitable method for measuring peak areas.

1.8 Volumetric Flasks: Convenient sizes for preparing standard solutions.

1.9 Pipets: Convenient sizes for preparing standard solutions and 15 ml pipets for measuring the collection medium.

1.10 Teflon tubing (15 cm long x 7 mm I.D.) and Teflon plugs for sealing the inlet and outlet of the bubbler stem before shipping.

2. REAGENTS

Whenever possible, all reagents used must be ACS reagent grade or better.

2.1 Maleic anhydride, ±99%. Note: Maleic anhydride will slowly hydrolyze in the presence of humid air. Care should be taken to protect it from humid conditions.

2.2 Deionized and distilled water.

2.3 Dicylohexylamine

2,4 Formic acid

2.5 Methanol. HPLC grade

2.6 HPLC Mobile Phase

2.6.1 Add 10 ml of dicyclohexylamine and 10 ml of formic acid to 100 ml volumetric flask. Bring to volume with distilled water.

2.6.2 Add 10 ml of the solution prepared in Section 7.6.1 and 250 ml of methanol to a 1 litre volumetric flask. Bring this solution to volume with distilled water. Filter and degas prior to use.

2.7 Acetone

2.8 Stock Maleic Anhydride Standard Solution. Prepare a 1.08 mg/ml stock solution of maleic anhydride in acetone.

3. PROCEDURE

3.1 Cleaning of Equipment. See Method 1a.

3.2 Collection of Samples

3.2.1 Pipet 15 ml of distilled water into a midget bubbler, and mark the liquid level before inserting the bubbler frit. Be sure that the bubbler frit is completely immersed in the water. If the water does not cover the frit, do not use the bubbler. Maleic anhydride will not be collected efficiently unless the bubbler frit is completely immersed in the water.

3.2.2 Connect the outlet of the midget bubbler to the trap's inlet.

3.2.3 Air being sampled should not pass through any hose or tubing before entering the bubbler.

3.2.4 A sample size of 360 litres is recommended. Sample at a flow rate of 1.5 litres per minute. The flow rate should be known with an accuracy of $\pm$5%.

3.3 Analysis of Samples

3.3.1 Remove the bubbler stem from the bubbler. Allow water to drain from the frit into the bubbler. If the sample volume is less than 15 ml, add water until the volume reached the 15 ml mark.

3.3.2 HPLC Conditions. The typical operating conditions for the HPLC are:

Column Temperature:	Ambient
Flow Rate:	1.7 ml/minute
Mobile Phase:	1% PIC reagent (Section 7.6.1)/ 25% methanol/74% distilled water
Detector:	UV photometer at 254 nm
Retention Time:	6 minutes

During the experimental study, all samples and blanks contained a peak eluting after maleic acid (at about 8 minutes) which was believed to be phthalic acid.

3.3.3 Injection: The chromatograph is fitted with a sample injection valve and a 50 microlitre sample loop. Flush this loop thoroughly with the sample (500 microlitres) and inject the sample.

4. CALCULATIONS

4.1 Read the weight, in micrograms, corresponding to each peak area from the appropriate standard curve. No volume correction is needed if the standard curve is based on micrograms/ 15 ml of distilled water and the volume of sample injected is identical to the volume of the standards injected. See Method 1a for computation of results.

5. REFERENCES

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5.2 Backup Data Report No. 302 for Maleic Anhydride prepared under NIOSH Contract No. 210-76-0123.

METHOD 34

(METHYL ACRYLATE)

Method Ref:	34 (NIOSH S38)
Range:	13.9 to 58.4 mg/m^3
Precision:	$(\overline{CV}_T)$ 0.066
Procedure:	Adsorption on charcoal, desorption with carbon disulfide, GC

1. APPARATUS

1.1 A calibrated personal sampling pump.

1.2 Charcoal tubes: See Method 1a.

1.3 Gas chromatograph equipped with a flame ionization detector.

1.4 Column (10 ft x 1/8 in I.D. stainless steel) packed with 5% FFAP stationary phase on 100/120 mesh Supelcoport.

1.5 An electronic integrator or some other suitable method for measuring peak areas.

1.6 Two millilitre sample containers with glass stoppers or Teflon-lined caps. If an automatic sample injector is used, the associated vials may be used.

1.7 Microlitre syringes: 10 µl, and other convenient sizes for making standards.

1.8 Pipets: 1.0 ml type graduated in 0.1 ml increments.

1.9 Volumetric flasks: 10 ml or convenient sizes for making standard solutions.

2. REAGENTS

2.1 Chromatographic quality carbon disulfide

2.2 Methyl Acrylate, reagent grade

2.3 Undecane, or other suitable internal standard

2.4 Purified helium

2.5 Prepurified hydrogen

2.6 Filtered compressed air

METHOD 34

(METHYL ACRYLATE)

(cont'd)

3. PROCEDURE

3.1 Cleaning of equipment. See Method 1a.

3.2 Calibration of Personal Pumps. See Method 1a.

3.3 Collection of Samples

3.3.1 A maximum sample size of 5 litres is recommended. Sample at a rate of 0.2 litres per minute or less. The flow rate should be known with an accuracy of at least ±5%. See Method 1a.

3.4 Analysis of Samples

3.4.1 Preparation of Samples. See Method 1a.

3.4.2 Desorption of Samples: Prior to analysis, 1.0 ml of carbon disulfide is pipetted into each sample container. Desorption should be done for 30 minutes.

3.4.3 GC Conditions: The typical operating conditions for the gas chromatograph are:

1. 30 ml/min (60 psig) helium carrier gas flow
2. 35 ml/min (25 psig) hydrogen gas flow to detector
3. 400 ml/min (60 psig) air flow to detector
4. 225°C injector temperature
5. 250°C manifold temperature (detector)
6. 70°C column temperature

3.4.4 Injection. A 5.0 µl aliquot is injected.

4. CALCULATIONS

4.1 Read the weight, in mg, corresponding to each peak area from the standard curve. No volume corrections are needed, if the standard curve is based on mg per 1.0 ml carbon disulfide and the volume of sample injected is identical to the volume of the standards injected. See Method 1a for computation of results.

5. REFERENCES

5.1 White, L.D., et al, "A Convenient Optimized Method for the Analysis of Selected Solvent Vapors in the Industrial Atmosphere", Amer. Ind. Hyg. Assoc. J., 31: 225 (1970).

5.2 Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.

5.3 Final Report, NIOSH Contract HSM-99-71-31, "Personal Sampler Pump for Charcoal Tubes", 15 September 1972.

METHOD 35

(METHYL CHLORIDE)

Method Ref:	35 (NIOSH S99)
Range:	59 to 220 ppm (8 hr. T.W.A.)
	143 to 589 ppm (Peak)
Precision:	$(\overline{CV}_T)$ 0.052
Procedure:	Adsorption on charcoal, desorption with methylene chloride, GC

1. APPARATUS

1.1 Personal Sampling Pump

1.2 Charcoal Tubes: Two charcoal tubes are used in this method. One charcoal tube is used to collect the samples and a small charcoal tube is used as a backup. The charcoal tubes are connected in series with Tygon tubing. The larger charcoal tube is a glass tube, approximately 10 cm long with a 8 mm O.D. and 6 mm I.D. It has two sections of 20/40 mesh activated coconut charcoal separated by a 2 mm portion of urethane foam. The front section contains 400 mg of charcoal; the back section contains 200 mg. A 3 mm portion of urethane foam is placed between the outlet end of the tube and the backup section. A plug of silylated glass wool is placed in front of the absorbing section. The smaller charcoal tube contains 100 mg of charcoal in the front section and 50 mg in the backup section.

1.3 Gas chromatograph equipped with a flame ionization detector.

1.4 Column (4 ft long x 1/4 in O.D. stainless steel) packed with 80/100 mesh Chromosorb 102.

1.5 An electronic integrator or some other suitable method for measuring peak areas.

1.6 Microlitre Syringes: 10 microlitre for injection of samples into the gas chromatograph.

1.7 Gas Tight Syringes: 0.1, 0.25, 0.50 and 1.0 ml sizes for preparing standards.

1.8 Pipets: 3.0 ml delivery pipets.

1.9 Serum Bottles: 15 ml glass bottles with 20 mm O.D. mouth. Septa: 20 mm rubber septa with Teflon lining. Aluminum tear-away seals to fit serum bottles.

1.10 Hand crimper for sealing septa to serum bottles.

1.11 Stopwatch

1.12 Manometer

2. REAGENTS

2.1 Methylene chloride, chromatographic quality, methyl chloride-free.

2.2 Methyl chloride, 99.5%.

2.3 Purified nitrogen

2.4 Prepurified hydrogen

2.5 Filtered compressed air

3. PROCEDURE

3.1 Cleaning of Equipment. See Method 1a.

3.2 Calibration of Sampling Pumps. See Method 1a.

3.3 Collection of Samples

3.3.1 Air should flow through the large charcoal tube before entering the small charcoal tube. See Method 1a.

3.3.2 For peak concentration measurement, a sample size of 0.5 l is recommended. Sample for 5 minutes at a flow rate of 0.10 l/min.

3.4 Analysis of Samples

Upon receipt of samples in the laboratory, the samples should be refrigerated if analysis cannot be done immediately.

3.4.1 Desorption of Methyl Chloride. Pipet 3.0 ml of methylene chloride into the 15 ml serum bottle. Remove the plastic caps from both ends of the larger charcoal tube. Remove the plug of urethane foam from the outlet end of the tube. Transfer the 200 mg portion of charcoal to the serum bottle. Next, remove the glass wool plug from the inlet end of the tube and transfer the 400 mg section of charcoal to the

same bottle. Place the Teflon-lined septum over the mouth of the bottle and seal the aluminum seal on with the crimper. It is important that the transfer of the charcoal be carried out as quickly as possible once the methylene chloride has been added to the bottle. The backup charcoal tube should be handled in a similar manner, using a separate serum bottle. The two samples are analyzed separately.

3.4.2 Gently shake the sample. The extract is now ready for analysis. Analysis should be completed within one day after the methyl chloride is desorbed. Fresh standards should be prepared daily (throughout the day if possible).

3.4.3 GC Conditions. The typical operating conditions for the gas chromatograph are:

1. 40 ml/min (60 psig) nitrogen carrier gas flow rate
2. 65 ml/min (24 psig) hydrogen gas flow rate to detector
3. 500 ml/min (50 psig) air flow rate to detector
4. 200°C injector temperature
5. 260°C detector temperature
6. 100°C column temperature

3.4.4 Injection. A 5.0 µl aliquot is injected.

4. CALCULATIONS

4.1 Read the weight, in mg, corresponding to each peak area from the standard curve. No volume corrections are needed if the standard curve is based on mg/3.0 ml methylene chloride and the volume of sample injected is identical to the volume of the standards injected. See Method 1a for computation of results.

5. REFERENCES

5.1 White. L.D., et al, "A Convenient Optimized Method for the Analysis of Selected Solvent Vapors in the Industrial Atmosphere", Amer. Ind. Hyg. Assoc. J., 31, 225 (1970).

5.2 Documentation of NIOSH Validation Tests, NIOSH Contract CDC-99-74-45.

5.3 Backup Data Report for Methyl Chloride, prepared under NIOSH Contract No. 210-76-0123.

5.4 Final Report, NIOSH Contract HSM-99-71-31, "Personal Sampler Pump for Charcoal Tubes", 15 September 1972.

METHOD 36

(MORPHOLINE)

Method Ref: 36 (NIOSH S150)
Range: 28.5 to 108.4 4 mg/m^3
Precision: ($\overline{CV}_T$) 0.057
Procedure: Adsorption on silica gel, desorption with 0.05 M sulfuric acid, GC

1. APPARATUS

1.1 A calibrated personal sampling pump.

1.2 Silica gel tubes. See method No. 1a.

1.3 Gas chromatograph equipped with a flame ionization detector.

1.4 Column (4 ft. long by 1/4 in. stainless steel) packed with 80/100 mesh Chromosorb 103. A 3 in. in Ascarite "precolumn" is inserted at the inlet end of the column and is separated from the Chromosorb 103 column packing by a plug of glass wool. The Ascarite "precolumn" should be checked periodically for salt buildup. The column should be baked out at 200°C at the end of each day, and the Ascarite "precolumn" should be changed at least once a month.

1.5 The GC inlet should have a removable glass liner that can be cleaned.

1.6 An electronic integrator or some other suitable method for measuring peak areas.

1.7 Two milliliter sample containers with glass stoppers or Teflon-lined caps.

1.8 Microliter syringes: 10 microliter, and other convenient sizes for making standards.

1.9 Pipets: 1.0 ml delivery pipets.

1.10 Volumetric flasks: 10 ml or convenient sizes for making standard solutions.

2. REAGENTS

2.1 Sulfuric acid, 0.05 M.

2.2 Sodium Hydroxide, 1.2 M.

2.3 Morpholine, reagent grade.

2.4 n-Hexane, reagent grade

2.5 Prepurified hydrogen

2.6 Filtered compressed air

2.7 Purified nitrogen

2.8 pH paper - Hydrion.

3. PROCEDURE

3.1 Cleaning of Equipment. See method no. 1a.

3.2 Calibration of Personal Pumps. See method no. 1a.

3.3 Collection of Samples

3.3.1 A sample size of 20 litres is recommended. Sample at a flow of 0.2 litres per minute or less. The flow rate should be known with an accuracy of at least ±15%. See method no. 1a.

3.4 Analysis of Samples.

3.4.1 Preparation of Samples. See method no. 1a.

3.4.2 Desorption of Samples. Prior to analysis, 1.0 ml of 0.05 M sulfuric acid is pipetted into each sample container. The sample is desorbed for 30 minutes. Transfer a 0.5 ml aliquot of the desorbed sample to a new vial, and add 50 microlitres of 1.2 M sodium hydroxide to make the solution alkaline. Mix the solution well. The pH of the resulting solution should be greater than 10 as indicated with pH paper. This solution should be analyzed immediately to avoid loss of the volatile analyte which is present as a free base.

3.4.3 GC Conditions. The typical operating conditions for the gas chromatograph are:

1. 50 ml/min (60 psig) nitrogen carrier gas flow
2. 65 ml/min (24 psig) hydrogen gas flow to detector
3. 500 ml/min (500 psig) air flow to detector
4. 250°C injector temperature
5. 280°C manifold temperature (detector)
6. 200°C column temperature

3.4.4 Injection. A 5.0 µl aliquot is withdrawn.

4. CALCULATIONS

4.1 Read the weight, in mg, corresponding to each peak area from the standard curve. No volume corrections are needed if the standard curve is based on mg/1.0 ml 0.05 M sulfuric acid basified with 100 microlitres of 1.2 M sodium hydroxide and the volume of sample injected is identical to the volume of the standards injected.

5. REFERENCES

1. Evan E. Campbell, Gerry O. Wood, and Robert G. Anderson, "Development of Air Sampling Techniques, Los Alamos Scientific Laboratory Progress Reports" LA-5634PR (June 1974), LA-5973-PR (July 1975), LA-6057-PR (September 1975).

2. C.E. Andre and A.R. Mosier, "Precolumn Inlet System for the Gas Chromatographic Analysis of Trace Quantities of Short-Chain Aliphatic Amines", Analytical Chemistry 45, 1971-1973 (1973).

3. Documentation of NIOSH Validation Tests, NIOSH Contract CDC99-74-45.

4. Final Report, NIOSH Contract HSM-99-71-31, "Personal Sampler Pump for Charcoal Tubes", September 15, 1972.

METHOD 37

(NAPHTHA, COAL TAR)

Method Ref: 37(NIOSH S86)
Range: 193 to 809 mg/m^3
Precision: $(\overline{CV}_T)$ 0.051
Procedure: Adsorption on charcoal, desorption with carbon disulfide, GC

1. APPARATUS

1.1 A calibrated personal sampling pump.

1.2 Charcoal tubes: See method No. 1a.

1.3 Gas chromatograph equipped with a flame ionization detector.

1.4 Column (6 ft. x 1/8 in. I.D. stainless steel) packed with 1.5% OV-101 on 100/120 mesh Chromosorb W.

1.5 An electronic integrator or some other suitable method for measuring peak areas.

1.6 Two-millilitre sample containers with glass stoppers or Teflon-lined caps. If an automatic sample injector is used, the associated vials may be used.

1.7 Microlitre syringes: 10-microlitre, and other convenient sizes for making standards.

1.8 Pipets: 1.0 ml type graduated in 0.1 ml increments.

1.9 Volumetric flasks: 10 ml or convenient sizes for making standard solutions.

2. REAGENTS

2.1 Chromatographic quality carbon disulfide.

2.2 Napththa, Coal tar (Boiling range: 154-195°C)

2.3 Undecane, or other suitable internal standard.

2.4 Purified helium

2.5 Prepurified hydrogen.

2.6 Filtered compressed air.

3. PROCEDURE

3.1 Cleaning of equipment. See method No. 1a. Analysis should be detergent washed and thoroughly rinsed with tap water and distilled water.

3.2 Calibration of Personal Pumps. See method No. 1a.

3.3 Collection of Samples.

3.3.1 A maximum sample size of 10 litres is recommended. Sample at a rate of 0.2 litres per minute or less. The flow rate should be known with an accuracy of at least $\pm$5%.

3.4 Analysis of Samples.

3.4.1 Preparation of Samples. See method No. 1a.

3.4.2 Desorption of Samples. Prior to analysis, 1.0 ml of carbon disulfide is pipetted into each sample container. Desorption should be done for 30 minutes.

3.4.3 GC Conditions. The typical operating conditions for the gas chromatograph are:

1. 30 ml/min (60 psig) Helium carrier gas flow
2. 35 ml/min (25 psig) Hydrogen gas flow to detector
3. 400 ml/min (60 psig) Air flow to detector
4. 225°C injector temperature
5. 250°C manifold temperature (detector)
6. 80°C column temperature

3.4.4 Injection. A 50 µl aliquot is injected.

4. CALCULATIONS

4.1 Read the weight, in mg, corresponding to each total peak area from the standard curve. No volume corrections are needed, if the standard curve is based on mg per 1.0 ml carbon disulfide and the volume of sample injected is identical to the volume of the standards injected. See method No. 1a.

5. REFERENCES

1. White, L.D. et al - "A Convenient Optimized Method for the Analysis of Selected Solvent Vapors in the Industrial Atmosphere", Amer. Ind. Hyg. Assoc., J., 31: 225 (1970).

2. Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.

3. Final Report, NIOSH Contract HSM-99-71-31, "Personal Sampler Pump for Charcoal Tubes", September 15, 1972.

METHOD 38

(NAPHTHALENE)

Method Ref: 38(NIOSH S292)
Range: 19.3 to 83 mg/m^3
Precision: ($\overline{CV}_T$) 0.055
Procedure: Adsorption on charcoal, desorption with carbon disulfide, GC

1. APPARATUS

1.1 A calibrated personal sampling pump. See method no. 1a.

1.2 Charcoal tubes. See method No. 1a.

1.3 Gas chromatograph equipped with a flame ionization detector.

1.4 Column (10 ft. x 1/8 in. I.D. stainless steel) packed with 10% OV-101 stationary phase on 100/120 mesh Supelcoport.

1.5 An electronic integrator or some other suitable method for measuring peak areas.

1.6 Two-millilitre sample containers with glass stoppers or Teflon-lined caps. If an automatic sample injector is used, the associated vials may be used.

1.7 Microlitre syringes: 10 microlitre, and other convenient sizes for making standards.

1.8 Pipets: 1.0 ml type graduated in 0.1 ml increments.

1.9 Volumetric flasks: 10 ml or convenient sizes for making standard solutions.

2. REAGENTS

2.1 Chromatographic quality carbon disulfide.

2.2 Naphthalene, reagent grade.

2.3 Undecane, or other suitable internal standard.

2.4 Purified nitrogen.

2.5 Prepurified hydrogen.

2.6 Filtered compressed air.

METHOD 38

(NAPHTHALENE)

(cont'd)

3. PROCEDURE

3.1 Cleaning of Equipment. See method No. 1a.

3.2 Calibration of Personal Pumps. See method No. 1a.

3.3 Collection of Samples.

3.3.1 A maximum sample size of 200 litres is recommended. Sample at a rate of 1.0 litre per minute or less. The flow rate should be known with an accuracy of at least $\pm$ 5%.

3.4 Analysis of Samples.

3.4.1 Preparation of Samples. See method No. 1a.

3.4.2 Desorption of Samples. Prior to analysis, 1.0 ml of carbon disulfide is pipetted into each sample container. Desorption should be done for 30 minutes.

3.4.3 GC Conditions. The typical operating conditions for the gas chromatograph are:

1. 30 ml/min (60 psig) Nitrogen carrier fas flow
2. 35 ml/min (25 psig) Hydrogen gas flow to detector
3. 400 ml/min (60 psig) Air flow to detector
4. 225°C injector temperature
5. 250°C manifold temperature (detector)
6. 125°C column temperature

3.4.4 Injection. A 5.0 µl aliquot is injected.

4. CALCULATIONS

4.1 Read the weight, in mg, corresponding to each peak area from the standard curve. No volume corrections are needed, if the standard curve is based on mg per 1.0 ml carbon disulfide and the volume of sample injected is identical to the volume of the standards injected. See method No. 1a for computation of results.

5. REFERENCES

1. White, L.D. et al, "A Convenient Optimized Method for the Analysis of Selected Solvent Vapors in the Industrial Atmosphere", Amer. Ind. Hyg. Assoc. J., 31: 225 (1970).

2. Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.

3. Final Report, NIOSH Contract HSM-99-71-31, "Personal Sampler Pump for Charcoal Tubes", September 15, 1972.

METHOD 39

(PENTACHLOROPHENOL)

Method Ref: 39 (NIOSH S297)
Range: 0.265 to 1.130 mg/m^3
Precision: ($\overline{CV}_T$) 0.072
Procedure: Filter and bubbler collection, ethylene glycol extraction, HPLC

1. APPARATUS

1.1 Filter Units. The filter unit consists of a 37 mm diameter cellulose ester membrane filter (Millipore Type AA or equivalent) with a pore size of 0.80 micrometer, supported by a stainless steel screen on a 37 mm three-piece filter holder. It is important that a stainless steel screen be used since other filter supports may retain part of the vapour.

1.2 Flexible Teflon or polyethylene tubing to connect the holder to the bubbler.

1.3 A glass midget bubbler containing 15 ml of ethylene glycol.

1.4 Personal Sampling Pump.

1.5 Barometer.

1.6 Thermometer.

1.7 High performance liquid chromatograph capable of UV detection at a wavelength of 254 nm and a sample injection valve with a 20 nm external sample loop.

1.8 Column (30 cm x 3.9 mm I.D. stainless steel) packed with µBondapak C_{18}. The porous packing material consists of silica particles with a bonded coating of C_{18} organosilane. This packing can be obtained from Waters Associates, Milford, Massachusetts.

1.9 An electronic integrator or some other suitable method for measuring peak areas.

1.10 Tweezers

1.11 Microliter syringes, 50 and 100 microliter.

1.12 Volumetric flasks, convenient sizes for preparing standard solutions.

1.13 Pipets, convenient sizes for preparing standard solutions and 10 and 15 ml pipets for measuring the extraction medium.

1.14 Teflon tubing (15 cm long x 7 mm I.D.) or Teflon plugs for sealing the inlet and outlet of the bubbler stem before shipping.

2. REAGENTS

All reagents used must be ACS reagent grade or better.

2.1 Pentachlorophenol.

2.2 Dowicide EC-7 (purified pentachlorophenol).

2.3 Ethylene glycol.

2.4 Methanol, distilled in glass.

2.5 Isopropanol.

2.6 Deionized, distilled water.

3. PROCEDURE

3.1 Cleaning of Equipment. See method No. 1a.

3.2 Calibration of Personal Sampling Pumps. See method No. 1a.

3.3 Collection of Samples.

3.3.1 Assemble the filter in the three-piece filter holder and close firmly. The filter is backed up by a stainless steel screen. Secure the filter holder together with tape or shrinkable band.

3.3.2 Pipet 15 ml of ethylene glycol into each midget bubbler, and mark the liquid level. Be sure that the bubbler frit is completely immersed in the ethylene glycol.

3.3.3 Remove the filter holder plugs and attach the outlet of the filter holder to the inlet arm of the midget bubbler using a short piece of flexible polyethylene or Teflon tubing. Connect the outlet arm of the midget bubbler to a second empty bubbler and then to the personal sampling pump, using short pieces of flexible tubing. The bubblers must be maintained in a vertical position during sampling.

3.3.4 Air being sampled should not pass through any hose or tubing before entering the filter holder.

3.3.5 A sample size of 180 litres is recommended. Sample at a flow rate of 1.5 litres per minute. The flow rate should be known to within ± 5%.

3.4 Analysis of Samples:

3.4.1 If the sample volume is less than 15 ml, add ethylene glycol until the volume reaches the 15 ml mark. If the sample volume is more than 15 ml, determine the volume and make an appropriate volume correction in the calculations indicated in Section 10.1.

3.4.2 Add 10 ml of methanol to each sample just before analysis and mix the solution gently but thoroughly.

3.4.3 HPLC Conditions. The typical operating conditions for the high pressure liquid chromatograph are:

1.	Column Temperature:	Ambient
2.	Column Pressure:	2300 psi
3.	Flow Rate:	1.6 ml/min
4.	Mobile Phase:	60% methanol/40% water (V/V)
5.	Detector:	UV photometer at 254 nm
6.	Capacity Ratio:	1.8

3.4.4 Injection. The first step in the analysis is to inject the sample into the high pressure liquid chromatograph. The chromatograph is fitted with a sample injection valve and a 20 microliter sample loop. Flush this loop thoroughly with solvent (300 microliters), then fill the loop with sample solution and inject.

4. CALCULATIONS

4.1 Read the weight, in µg/25 ml, corresponding to each peak area from the appropriate standard curve. No volume correction is needed, if the standard curve is based on µg/25 ml of ethylene glycol/methanol and the volume of sample injected is identical to the volume of the standards injected. See method No. 1a.

5. REFERENCES

1. Documentation of NIOSH Validation Tests, National Institute for Occupational Safety and Health, Cincinnati, Ohio (DHEW/ NIOSH-Publication No. 77-185), 1977. Available from Superintendent of Documents, U.S. Government Printing Office, Washington, D.C., Order No. 017-033-00231-2.

2. Backup Data Report for Pentachlorophenol, prepared under NIOSH Contract No. 210-76-0213.

METHOD 40

(PHENOL)

Method No:	40 (NIOSH S330)
Range:	9.46 to 37.8 mg/m^3
Precision:	(CV_T): 0.068
Procedure:	Bubbler Collection in dilute sodium hydroxide: GC analysis of the collected samples after acidification with sulfuric acid.

1. APPARATUS

1.1 Sampling Equipment. The sampling unit for the bubbler collection method consists of the following components:

1.1.1 A standard glass midget bubbler containing the collection medium (Section 2.4).

1.1.2 A pump suitable for delivering at least 1 litre per minute for 100 minutes. The sampling pump is protected from splash-over or solvent condensation by a 5 cm long by 6 mm I.D. glass tube loosely packed with a plug of glass wool and inserted between the exit arm of the bubbler and the pump.

1.1.3 An integrating volume meter such as a dry gas or wet test meter.

1.1.4 Thermometer

1.1.5 Manometer

1.1.6 Stopwatch

1.2 Gas chromatograph equipped with a flame ionization detector.

1.3 Column (4 ft. long x 1/4 in. O.D. stainless steel) packed with 35/60 mesh Tenax.

1.4 An electronic integrator or some other suitable method for measuring peak areas.

1.5 Microliter syringes: 10-microliter, and other convenient sizes for making standards and injecting samples into the GC.

1.6 Volumetric flasks: convenient sizes for making solutions.

1.7 Pipets: 15 ml or other convenient sizes.

METHOD 40

(PHENOL)

(cont'd)

2. REAGENTS

2.1 Distilled water.

2.2 Phenol, reagent grade.

2.3 Sulfuric acid, reagent grade.

2.4 Collection medium, 0.1 N sodium hydroxide. Dissolve 4.0 g of sodium hydroxide in distilled water and dilute to a final volume of 1 litre.

2.5 Purified nitrogen

2.6 Purified hydrogen

2.7 Filtered compressed air

3. PROCEDURE

3.1 Cleaning of Equipment. See method No. 1a.

3.2 Calibration of Personal Sampling Pumps. Each pump should be calibrated by using an integrating volume meter or other means.

3.3 Collection of Samples:

3.3.1 Pour 15 ml of the collection medium (Section 2.4) into each midget bubbler.

3.3.2 Connect the midget bubbler with a 5 cm glass absorption tube (6-mm I.D. AND 8-mm O.D.) containing the glass wool plug, then to the personal sampling pump using short pieces of flexible tubing. The air being sampled should not pass through any tubing or other equipment before entering the bubbler.

3.3.3 Turn the pump on to begin sample collection. The sample should be taken at a flow rate of 1 litre per minute. A sample size of 100 litres is recommended.

3.4 Analysis of Samples.

3.4.1 The sample in each bubbler is analyzed separately.

3.4.2 Transfer the solution to a 25 ml volumetric flask.

3.4.3 Rinse the bubbler twice with 1 ml of distilled water and add the rinses to the flask.

3.4.4 Add 0.1 ml of concentrated sulfuric acid to the flask and mix. Check with pH paper to make sure that the pH is less than 4.

3.4.5 Dilute to mark with distilled water and mix.

3.4.6 GC Conditions. The typical operating conditions for the gas chromatograph are:

1. 50 ml/min (60 psig) nitrogen carrier gas flow
2. 65 ml/min (24 psig) hydrogen gas flow to detector
3. 500 ml/min (50 psig) air flow to detector
4. 215°C injector temperature
5. 225°C manifold temperature (detector)
6. 200°C column temperature

3.4.7 Injection. Inject a 5.0 µl aliquot into G.C.

3.5 Standard Solutions:

3.5.1 Procedure for preparing standard solutions. Six standards at each of the three levels (0.5X, 1X, and 2X the OSHA standard) are prepared by introducing a known amount of analyte into 15 ml of 0.1 N sodium hydroxide in a 25 ml volumetric flask. The amount introduced is equivalent to that present in a 1 litre air sample. The standards are acidified with 0.1 ml of concentrated sulfuric acid and made up to volume with distilled water. The solution should be checked with pH paper to make sure that its pH is less than 3. A parallel blank is prepared in the same manner, except that no analyte is added. The standards and blank are analyzed in exactly the same manner as the samples in Section 8.4.

4. CALCULATIONS

4.1 Read the weight, in mg, corresponding to each peak area from the standard curve. No volume corrections are needed if the standard curve is based on mg/sample and the volume of sample injected is identical to the volume of the standard injected.

5. REFERENCE

1. Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.

METHOD 41

(PHOSPHORIC ACID)

Method No:	41 (P & CAM 216 or NIOSH S333)
Range:	0.47 to 1.93 mg/m^3
Precision:	$(\overline{CV}_T)$ 0.055
Procedure:	Filter collection, Water leach, complex formation, colorimetric

1. APPARATUS

1.1 Sampling equipment - The sampling unit for the collection of personal air samples for the determination of inorganic aerosol has the following components:

1.1.1 The filter unit consisting of the filter media (Section 1.2) and appropriate 37 mm 3-piece cassette filter holder.

1.1.2 Personal Sampling Pump:

1.1.3 Thermometer

1.1.4 Manometer

1.1.5 Stopwatch

1.2 Mixed cellulose ester membrane filter, 0.8 micrometer pore size and 37 mm diameter. The filter is held in the three piece cassette supported by a cellulose backup pad.

1.3 Spectrophotometer, capable of reading at 830 nm.

1.4 Matched glass cells or cuvettes, 1 cm path length.

1.5 Boiling water bath.

1.6 Steambach, or equivalent, maintained at 85-100°C.

1.7 Phillips beakers, 125 ml.

1.8 Assorted laboratory glassware: pipets, volumetric flasks, watchglasses.

2. REAGENTS

All reagents must be ACS Reagent grade or better.

2.1 Distilled water

2.2 Potassium dihydrogen phosphate solution. Dissolve 0.1389 g of potassium dihydrogen phosphate, KH_2PO_4, in distilled water and dilute to one litre. 1 ml = 100 µg phosphoric acid, H_3PO_4.

2.3 Sodium molybdate solution. Dissolve 25.0 g of sodium molybdate, $Na_2MoO_4 . 2H_2O$, in 10 N sulfuric acid and dilute to one litre with 10 N sulfuric acid.

2.4 Hydrazine sulfate solution. Dissolve 1.5 g of hydrazine sulfate, $N_2H_6SO_4$, in distilled water and dilute to one litre.

3. PROCEDURE

3.1 Cleaning of glassware. Contamination of glassware by detergents should be guarded against, especially when small amounts of phosphorus are being determined. Many detergents contain phosphates. Glassware that may have been cleaned with such detergents should be boiled in 1:1 hydrochloric acid and rinsed carefully.

3.2 Calibration of personal pumps. See method No. 1a.

3.3 Collection of Samples:

3.3.1 A sample size of 90 litres is recommended. Sample at a flow rate of 1.5 litres per minute. The flow rate should be known with an accuracy of at least $\pm$ 5%.

3.4 Analysis of Samples:

3.4.1 Open the cassette filter holder and carefully remove the 10 ml distilled water, cover with a watchglass and place on a steambath or equivalent for 10 minutes. Decant the water into a 50 ml volumetric flask and repeat with another 10 ml of distilled water. Rinse the inside of the beaker with an additional 5 ml of distilled water and transfer quantitatively to the 50 ml volumetric flask.

3.4.2 Pipet 5 ml of the sodium molybdate solution and 2 ml of the hydrazine sulfate solution into the volumetric flask. Dilute to the mark with distilled water and shake well.

3.4.3 Immerse the volumetric flask in a boiling water bath for 10 minutes. Remove and cool rapidly to room temperature.

3.4.4 Read the absorbance in a spectrophotometer at 830 nm against a reagent blank prepared in the same manner as the samples.

4. CALIBRATION AND STANDARDS

4.1 Pipet into six 50 ml volumetric flasks 0, 0.25, 0.5, 1.0, 1.5, and 2.0 ml of the potassium dihydrogen sulfate solution.

4.2 Proceed as directed in Section 3.4.3.

4.3 Construct a calibration curve by plotting absorbance against the equivalent concentration of phosphoric acid in µg/50 ml.

5. CALCULATIONS

5.1 Determine from the calibration curve (Section 4.3) the µg concentration of phosphoric acid present in each sample. No volume corrections are needed since both the samples and standards are in 50 ml total volume.

6. REFERENCES

1. Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.

2. P & CAM 216, Phosphoric Acid in Air.

3. M. Halmann, "Analytical Chemistry of Phosphorous Compounds", Vol. 37 of Chemical Analysis series by Elving and Kolthoff, John Wiley - Interscience, N.Y., 1972.

METHOD 42

(PHOSPHORUS IN AIR)

Method No: 42 (P & CAM 242 or NIOSH S334)
Range: 0.056 to 0.244 mg/m^3
Precision: 0.033 RSD (analytical)
Procedure: Filter/impinger (xylene) collection, FPD gas chromatography

1. APPARATUS

1.1 Sampling Equipment. The sampling unit for the impinger collection method consists of the following components:

1.1.1 A prefilter unit that consists of the filter medium and cassette filter holder.

1.1.2 A set of two midget impingers containing the absorbing solvent.

1.1.3 A pump suitable for delivering desired flow rates. The sampling pump is protected from solvent condensation by a tube loosely packed with a plug of fine glass wool and inserted between the exit arm of the impinger and the pump.

1.1.4 An integrating volume meter such as a wet test meter or dry gas meter.

1.1.5 Thermometer

1.1.6 Manometer

1.1.7 Stopwatch

1.2 Filter cassette with glass-fibre filter, 0.8 µm, 37 mm.

1.3 Forceps

1.4 Beakers, 100 ml

1.5 Volumetric flasks for standards.

1.6 Volumetric pipet, 10 ml.

1.7 Pipet bulb, rubber.

1.8 Perkin-Elmer 3920-b gas chromatograph, or equivalent with attendant equipment, including a phosphorus flame photometric detector.

1.9 Gas chromatography column constructed from 6 ft. x 4 mm I.D. silanized borosilicate glass or 6 ft. x 2 mm I.D. borosilicate glass packed with one of the following:

1.9.1 3% SE-30 on 80/100 mesh Gas Chrom Q

1.9.2 3% OV-1 on 100/120 mesh Gas Chrom Q

1.9.3 3.8% SE-30 on 80/100 mesh Chromosorb W-HP

1.9.4 3.0% SE-30 on 80/100 mesh Chromosorb W-HP

1.9.5 3% OV-1 on 100/120 mesh Chromosorb W-HP

1.9.6 4% DC-200 on 100/120 mesh Gas Chrom Q

Columns 1.9.4 and 1.9.5 are preferred. Columns 1.9.1 through 1.9.5 were conditioned by heating for one day at the recommended temperature under the appropriate carrier gas flow rate (30 ml/minute), then cooled to 170°C and treated with 10-50 µl of a silylation agent. The column may then be primed with 5 µl injections of 2 mg/ml phosphorus in xylene stock solution. Priming should only be performed when adequate column conditioning by silylation fails to provide the minimum detection limit.

1.10 Syringes, 5 µl, 10 µl and 100 µl.

1.11 Spatula, blade.

2. REAGENTS

2.1 Distilled water

2.2 Acetone, wash

2.3 Xylene, chromatoquality; this is absorbing solvent

2.4 Phosphorus (yellow, white), stick, 5/8-inch diameter, of known purity.

METHOD 42

(PHOSPHORUS IN AIR)

(cont'd)

3. PROCEDURE

3.1 Cleaning of Equipment. All glassware used should be scrupulously cleaned and given a final xylene rinse immediately before use. If colorimetric methods are to be used as secondary analysis, special cleaning should be performed with non-phosphate detergents.

3.2 Collection of Samples:

3.2.1 Pipette 10 ml of the absorbing solvent (Section 2) into the midget impinger.

3.2.2 Connect the impinger (via the adsorption tube) to the personal sampling pump and prefilter assembly with a short piece of flexible tubing. The minimum amount of tubing necessary to make the joint between the prefilter and the impinger should be used. The air being sampled should not be passed through any other tubing or equipment before entering the impinger.

3.2.3 Turn on the sampling pump to begin sample collection. Care should be taken to measure the flow rate, time and/or volume as accurately as possible. The sample should be taken at a flow rate of 0.5 to 1.0 L/min. A sample size of not more than 96 litres and no less than 24 litres should be collected. The minimum volume of air sampled will allow the measurement of at least 1/10 times the TLV, 0.01 mg/m^3 (760 mm Hg, 250^{o}C). A flow rate of 0.3 L/min may be employed where solvent evaporation appears significant; however, this is well below impinger flow/rate efficiency maximum.

3.3 Analysis of Samples:

3.3.1 The sample in 9 to 10 ml of xylene is transferred quantitatively to a 10 ml volumetric flask. Washings from the sample container are used to obtain exactly 10 ml solution.

3.3.2 Transfer the glass filter to a 100 ml beaker with a clean pair of forceps. Pipette 10 ml of xylene and agitate with a glass rod. Quantitatively transfer the xylene to a volumetric flask (10 ml) and dilute to the mark (if necessary).

3.3.3 Inject a 1 to 6 µl aliquot of the xylene solution, filter and impinger respectively, into the gas chromatograph and obtain a chromatogram. The chromatographic conditions are:

Column Temperature (6.9.1 to 6.9.5)	80°C
Injection port Temperature	200°C
Detector Temperature	200 - 225°C
Transfer line and switching valve (11.3)	235°C
Gas Carrier (He) Flow	80 ml/min 4 mm I.D. column 40 ml/min 2 mm I.D. column

Retention time of phosphine is approximately 0.3 minutes, whereas phosphorus retention time is greater than 3.0 minutes at these conditions.

4. CALIBRATION AND STANDARDS

4.1 Prepare at least four standard solution in the concentration range 100 mg/ml to 10,000 mg/ml from a stock solution of 2 mg/ml phosphorus in xylene. Should the samples be more concentrated than the most concentrated standard, then additional standards should be made until the samples are bracketed by standards.

4.2 Plot the amount (μg) of phosphorus seen by the detector versus the peak area (or peak height). A straight line passing through the origin should result.

5. CALCULATIONS

5.1 Determine the total amount, in μg, of phosphorus present in the filter and impinger separately and combine μg for total:

$$\mu g_f = \mu g_o \times \frac{\text{solution volume}}{\text{injection volume}}$$

$$\text{total } \mu g = \mu g_f + \mu g_i$$

where

μg_o = micrograms of phosphorus determined from calibration curve based on peak area (peak height) response

μg_f = micrograms of phosphorus on filter

μg_i = micrograms of phosphorus from impinger

solution volume = volume in microlitre (µl) of the final xylene solution (generally 10,000 µl)

injection volume = volume in µl of the aliquot of the final xylene solution injection into the gas chromatograph

5.2 Convert the volume of air sampled to standard conditions at 25°C and 760 mm Hg.

$$V_8 = V \times \frac{P}{760 \text{ mm Hg}} \times \frac{298^{\circ}C}{(273\ ^{\circ}C + T^{\circ}C)}$$

V_8 = volume of air in litres at 25°C and 760 mm Hg

V = volume of air in litres as measured

P = Barometric pressure in mm Hg

T = temperature of air in degrees centigrade

5.3 The concentration of phosphorus can be expressed in µg per litre or mg per m^3

$$mg/m^3 = \mu g/\text{litre}$$

$$mg/m^3 = \frac{\text{total } \mu g \text{ phosphorus}}{V_8}$$

6. REFERENCES

1. Barrett, W.J., H.K. Dillon, and R.H. James, "Development of Methods for the Determination of Elemental Phosphorus and Phosphine in Air", Third Bimonthly Report, HEW Contract No. 210-75-0047, January 30, 1976.

2. Bohl, C.D. and E.F. Kaelble, "Determination of Elemental Phosphorus in Air by Gas Chromatography", Am. Ind. Hyg. Assoc. J. 34:306, 1973.

3. Addison, R.F. and R.G. Ackman, "Direct Determination of Elemental Phosphorus by Gas-Liquid Chromatography", J. Chromatogr 47:421, 1970.

4. Burgett, C.A. and L.E. Green, "Improved Flame Photometric Detection without Solvent Flameout", J. Chromatogr. Sci. 12:356, 1974.

METHOD 43

(POLYCHLORINATED BIPHENYLS PCB)

Method No: 43 (P & CAM 244 OR NIOSH 244)
Range: 0.01 to 10 mg/m^3
Precision: 4.4% RSD (Analytical)
Procedure: Adsorption on Florisil, hexane desorption, gas chromatography with electron capture detection

1. APPARATUS

1.1 A personal-sampling pump which operates in the range of 50-200 cc/min is used.

1.2 Sorbent Tubes. Each glass tube is at least 7 cm long with 4 mm inside diameter and contains two sections of 30-48 mesh deactivated Florisil. The front section is preceded by glass wool and contains 100 mg and the backup section contains 50 mg. Urethane foam is placed between the sections and after the backup section. The ends of the tube are flame sealed to prevent contamination before use.

1.3 Gas chromatograph equipped with an electron capture detector (Ni^{63} foil).

1.4 Glass column (6 ft. x 4 mm I.D.) packed with 3% SE-30 or 3% OV-1 on 80/100 mesh Supelcoport of Gas Chrom Q.

1.5 Vials, 20-ml, with aluminum-lined caps.

1.6 Microlitre Syringe, 10 µl.

1.7 Volumetric flasks, 10 µl, with glass stoppers.

1.8 A mechanical or electronic integrator or a recorder and some method for determining peak area.

2. REAGENTS

ACS reagent grade or better.

2.1 Hexane, Pesticide Quality.

2.2 Florisil (Registered Trademark of the Floridin Co.), 30-48 mesh chromatographic adsorbent, deactivated. Florisil 30-60 mesh is sieved to the proper mesh size. Prior to packing tubes, dry a weighed amount of Florisil at 105°C for 45 minutes. After cooling to room temperature, the Florisil is added to a round bottom flask which can be attached to a rotary evaporator. Three millilitres of water per 100 gm of Florisil (i.e. 3 ml in 100 g is v/w) are added and the mixture is turned in the rotary evaporator for one hour or until it is free flowing.

2.3 Nitrogen, prepurified.

2.4 Standard PCB mixtures.

2.5 p,p-DDE (1,1-Dichloro-2,2-bis(p-chlorophenyl)ethene).

3. PROCEDURE

3.1 Cleaning of Equipment. All glassware used for the laboratory analysis should be detergent washed and thoroughly rinsed with tap water, distilled water, pesticide grade acetone, and finally pesticide grade hexane and dried.

3.2 Collection of Samples. See Method No.1a.

3.2.1 The air sample is taken at a flow rate of 200 cc/min or less to attain the total sample volume required. The recommended sample is 50 litres.

3.3 Analysis of Samples:

3.3.1 Preparation of Samples. See Method No.1a.

3.3.2 Desorption of Samples. Prior to analysis, 5.0 ml of hexane is pipetted into each vial. Florisil particles should not be allowed to cling to the glass above the solvent. A minimum of 10 minutes desorption time is required before analysis.

3.3.3 Gas Chromatographic conditions for PCB determination by the Standard Analytical Procedure are:

1. Nitrogen carrier gas flow, 90 ml/min
2. Injector temperature, 300°C
3. Interface and detector temperatures both 325°C
4. Column temperature, 200°C

3.3.4 Injection: A 5 µl aliquot is injected.

4. CALIBRATION AND STANDARDS

4.1 Standard Analytical Procedure. Standards are prepared in hexane at concentrations ranging from 8 to 500 ng/ml (within the linear range of the electron capture detector - upper limit is approximately 3 ng per injection). Calibration curves should be established daily since the electron capture detector response may vary from day to day. The standard curve is plotted in terms of concentration (ng/ml) versus area. Since the injection volumes of the standard and the sample are identical, the concentration of the sample can be read directly from the standard curve.

5. CALCULATIONS

5.1 Standard Analytical Procedure. The following are the steps in the calculation of air concentrations of PCB determined with PCB mixture as the standard.

5.1.1 The height or area of several selected prominent peaks (at least 5) in the chromatogram are added, compared to the total height or area of those same peaks in the standard, and the concentration of the sample solution is read from the standard curve.

5.1.2 The concentration, in ng/ml, of the sample solution is multiplied by the total volume, in ml, of the sample solution and the weight of the PCB in the sample is calculated. Corrections for the blanks are made if necessary.

5.1.3 The weights found on the front and the back sections of the tube are summed to find the total weight of the PCB in the air sample.

5.1.4 The total weight of the PCB in the air sample is divided by the volume, in litres, of air sampled and the air concentration is reported in ng/l or the equivalent units, g/m^3.

6. REFERENCES

1. Gian, C.A., H.S. Chan, and C.S. Neff, Anal Chem 47:2319, 1975.

2. Webb, R.G. and A.C. McCall, J. Chromarogr Sci 11:366, 1973.

3. Chau, A.S.Y. and R.C.J. Sampson, Environ Lett 8:89, 1975.

4. U.S. Environmental Protection Agency: Method for Polychlorinated Biphenyls (PCBs) in Industrial Effluents. Environment Monitoring Support Laboratory, EPA, Cincinnati, Ohio, 1973.

5. Hofstader, F.A., C.A. Bache, and D.J. Lisk, Bull Environ Contam Toxicol 11:136, 1974.

METHOD 44

(n-PROPYL ALCOHOL)

Method No: 44 (NIOSH S62)
Range: 225 to 835 mg/m^3
Precision: ($\overline{CV}_T$ 0.075)
Procedure: Adsorption on charcoal, desorption with effluent, GC

1. APPARATUS

1.1 A calibrated personal sampling pump.

1.2 Charcoal tubes: See Method No. 1a.

1.3 Gas chromatograph equipped with a flame ionization detector.

1.4 Column (10 ft. x 1/8 in. I.D. stainless steel) packed with 10% FFAP on 80/100 Chromosorb W-AW.

1.5 An electronic integrator or some other suitable method for determining peak size areas.

1.6 Two-millilitre glass sample containers with glass stoppers or Teflon-lined caps. If an automatic sample injector is used, the sample injector vials can be used.

1.7 Microlitre syringes: 10 µl, and other convenient sizes for making standards.

1.8 Pipets: 1.0 ml delivery type.

1.9 Volumetric flasks: 10 ml or convenient sizes for making standard solutions.

2. REAGENTS

2.1 Effluent: Carbon disulfide (chromatographic grade) containing 1% 2-propanol (reagent grade).

2.2 1-Propanol (reagent grade)

2.3 Internal Standard: n-Undecane (99+%) or other suitable standard.

2.4 n-Heptane (reagent grade)

2.5 Purified nitrogen

2.6 Prepurified hydrogen

2.7 Filtered compressed air

METHOD 44

(n-PROPYL ALCOHOL)

(cont'd)

3. PROCEDURE

3.1 Cleaning of Equipment. See Method No. 1a.

3.2 Calibration of Personal Pumps. See Method No. 1a.

3.3 Collection of Samples:

3.3.1 A maximum sample size of 10 litres is recommended. Sample at a flow of 0.20 litres per minute or less. The flow rate should be known with an accuracy of at least $\pm$ 5%.

3.4 Analysis of Samples.

3.4.1 Preparation of Samples. See Method No. 1a.

3.4.2 Desorption of Samples. Prior to analysis, 1.0 ml of the effluent is pipetted into each sample container. For the internal standard method, an 0.2 per cent solution of internal standard in the effluent is used.

3.4.3 GC Conditions. The typical operating conditions for the gas chromatograph are:

1. 30 ml/min (80 psig) nitrogen carried gas flow.
2. 30 ml/min (50 psig) hydrogen gas flow to detector.
3. 300 ml/min (50 psig) air flow to detector
4. 200°C injector temperature.
5. 300°C manifold temperature (detector)
6. 120°C column temperature

3.4.4 A 5.0 µl aliquot is injected.

4. CALCULATIONS

4.1 Read the weights, in mg, corresponding to each peak area (area ratio in case of the internal standard method) from the standard curve. No volume corrections are needed, if the standard curve is based on mg/ml effluent and the volume of sample injected is identical to the volume of the standards injected.

See Method No. 1a for computation of results.

5. REFERENCES

1. White, L.D., et al., "A Convenient Optimized Method for the Analysis of Selected Solvent Vapours in the Industrial Atmosphere", Amer. Ind. Hyg. Assoc. J.,31: 225 (1970).

2. "Documentation of NIOSH Validation Tests", Contract No. CDC-99-74-45.

3. Final Report, NIOSH Contract No. HSM-99-71-31, "Personal Sampler Pump for Charcoal Tubes, September 15, 1972".

METHOD 45

(PROPYLENE OXIDE)

Method No: 45 (NIOSH S75)
Range: 121 to 482 mg/m^3
Precision: ($\overline{CV}_T$) 0.085
Procedure: Adsorption on charcoal, desorption with carbon disulfide, GC

1. APPARATUS

1.1 A calibrated personal sampling pump. See Method No. 1a.

1.2 Charcoal tubes: glass tube with both ends flame sealed, 7 cm long with a 6 mm O.D. and a 4 mm I.D., containing 2 sections of 20/40 mesh activated charcoal separated by a 2 mm portion of urethane foam. The activated charcoal is prepared from coconut shells and is fired at 600°C prior to packing. The adsorbing section contains 100 mg of charcoal, the backup section 50 mg. A 3 mm portion of urethane foam is placed between the outlet end of the tube and the backup section. A plug of silylated glass wool is placed in front of the adsorbing section. The pressure drop across the tube must be less than one inch of mercury at a flow rate of 1 litre per minute.

1.3 Gas chromatograph equipped with a flame ionization detector.

1.4 Column (4 ft. x 1/4 in. I.D. stainless steel) packed with 50/80 mesh Porapak, Type Q.

1.5 An electronic integrator or some other suitable method for measuring peak areas.

1.6 One millilitre sample containers with glass stoppers or Teflon-lined caps.

1.7 Microlitre syringes: 10 microlitre, and other convenient sizes for making standards.

1.8 Pipets: 0.5 ml delivery pipets or 1.0 ml type graduated in 0.1 ml increments.

1.9 Volumetric flasks: 10 ml or convenient sizes for making standard solutions.

METHOD 45

(PROPYLENE OXIDE)

(cont'd)

2. REAGENTS

2.1 Chromatographic quality carbon disulfide.

2.2 Propylene Oxide, reagent grade.

2.3 Purified nitrogen

2.4 Prepurified hydrogen

2.5 Filtered compressed air

3. PROCEDURE

3.1 Cleaning of Equipment. See Method No. 1a.

3.2 Calibration of Personal Pumps. See Method No. 1a.

3.3 Collection of Samples:

3.3.1 A maximum sample size of 5 litres is recommended. Sample at a flow of 0.20 litres per minute or less. The flow rate should be known with an accuracy of at least $\pm$ 5%.

3.4 Analysis of samples:

3.4.1 Preparation of Samples. See Method No. 1a.

3.4.2 Desorption of Samples. Prior to analysis, 0.5 ml of carbon disulfide is pipetted into each sample container. Desorption should be done for 30 minutes.

3.4.3 GC Conditions. The typical operating conditions for the gas chromatograph are:

1. 50 ml/min (60 psig) nitrogen carrier gas flow
2. 65 ml/min (24 psig) hydrogen gas flow to detector
3. 500 ml/min (50 psig) air flow to detector
4. 190°C injector temperature
5. 255°C manifold temperature (detector)
6. 145°C column temperature

3.4.4 Injection. a 5.0 µl aliquot is injected.

4. CALCULATIONS

4.1 Read the weight, in mg, corresponding to each peak area from the standard curve. No volume corrections are needed, if the standard curve is based on mg/0.5 ml carbon disulfide and the volume of sample injected is identical to the volume of the standards injected.

5. REFERENCES

1. White, L.D., et al, "A Convenient Optimized Method for the Analysis of Selected Solvent Vapours in the Industrial Atmosphere, "Amer. Ind. Hyg. Assoc. J., 31 225 (1970).

2. Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.

3. Final Report, NIOSH Contract HSM-99-71-31, "Personal Sampler Pump for Charcoal Tubes", September 15, 1972.

METHOD 46

(SODIUM CYANIDE)

Method Ref:	46 (NIOSH S250)
Range:	2.62 to 9.68 mg/m^3
Precision:	$(\overline{CV_T})$ 0.103 (analytical)
Procedure:	Collection with filter and impinger, extraction with 0.1N NaOH, ion specific electrode.

1. APPARATUS

1.1 37 mm filter cassettes loaded with 0.8 µm pore size mixed cellulose ester filters.

1.2 Midget impingers filled with 10 ml of 0.1M of 0.1N NaOH solution.

1.3 Personal sampling pump(s) calibrated for a flow of 1.5 L.p.m. with the filter and impinger in line.

1.4 20 ml polyethylene screw cap bottles for transporting used impinger solution.

1.5 2 oz. squat ointment jars with aluminum lined screw caps for extracting the filters.

1.6 Orion 94-06 cyanide ion specific electrode or equivalent.

1.7 Orion 90-20-00 double junction reference electrode or equivalent.

1.8 pH meter with readout capacity in increments of 0.1 milliwatt.

1.9 Flow meter to calibrate sampling pump(s).

1.10 Associated sampling and laboratory equipment.

2. REAGENTS

2.1 All reagents must be ACS reagent grade or better.

2.2 Double distilled water.

2.3 Potassium cyanide.

2.4 0.1N sodium hydroxide.

2.5 1 L stock cyanide standard 200 mg CN/ml prepared by dissolving. 0.50 g KCN in 1L 0.1N NaOH .

2.6 6 working standards prepared daily from the stock solution in 25 ml quantities.

2.7 Lead acetate paper

2.8 Cadmium carbonate

3. PROCEDURE

3.1 All glassware should be thoroughly cleaned with strong detergent then rinsed carefully with warm tap water. The glassware is then rinsed with concentrated nitric acid, more tap water and finally distilled water. Particulate sodium cyanide is collected on a 37 mm mixed cellulose ester membrane. Hydrogen cyanide formed during sampling is collected in 0.1N NaOH in the impinger which is in series, after the filter, in the sampling train. The filters are extracted in 0.1N NaOH. The impinger solution and filter extracts are analyzed separately for cyanide with a cyanide ion specific electrode. The sum of the results of the two analyses represents the total sodium cyanide present.

Note: Gaseous hydrogen cyanide present in the atmosphere will interfere as it is also collected by the impinger. Since the method is not specific for sodium cyanide other particulate cyanides, potassium cyanide in particular, will be collected by the filter and interfere with the analysis.

3.2 Sample Collection:

3.2.1 The personal sampling pump is used to pull air through the filter and then through the impinger which is inserted in the sampling train in series with and immediately after the filter. A plug of glass wool should be loosely inserted in the tubing between the impinger and pump to protect the pump from splashback. The pump is calibrated to 1.5 L.p.m. with the filter and impinger in line. When the sampler is in place the pump should be run for 1 hour. The temperature and atmospheric pressure should be recorded for the sampling period to correct the sample volume if the conditions are significantly different from 25°C and 1 atmosphere. At the conclusion of sampling seal the filter cassette and transfer the impinger solution, quantitatively to a polyethylene vial. Wash the impinger stem with 2 ml of 0.1N NaOH and add this to the vial. One blank filter and impinger blank should be included with every ten samples.

3.3 Analysis:

3.3.1 Transfer the exposed filter to a 2 oz. ointment jar using tweezers, add 25 ml of 0.1N NaOH and cap. Allow the solution to stand for at least 30 minutes with occasional shaking. The extract should be analyzed within two hours of preparation. The impinger solution should be made up to 25 ml with the 0.1N NaOH prior to analysis. The electrodes and pH meter should be set up as per the user's manual. To analyze the solutions immerse the electrode in the solution. The solution should be stirred continuously with a magnetic stirrer during the reading. Blanks are analyzed in the same fashion and the result subtracted from the appropriate sample concentrations.

Note: The presence of sulphide ion will irreversibly poison the electrode. Sulphide can be removed by adding small amounts of powdered cadmium carbonate to the pH 11-13 solution until a drop of solution no longer discolours lead acetate paper. Large excesses of carbonate should be avoided as cadmium will complex the cyanide. Other metals which will complex cyanide are zinc, silver, nickel, cuprous, iron and mercury. The users manual for the electrode should be referred to if these are present in sufficient quantity. Bromide, chloride and iodide which form insoluble silver salts will cause the electrode to malfunction. Again, the users manual should be referred to if these are present.

4. CALIBRATION AND STANDARDS

4.1 Using the stock solution prepare six working solutions containing from 40-1000 µg CN in 25 ml of 0.1N NaOH. These standards should be prepared fresh each day and analyzed alternatively with the samples. To obtain a calibration curve plot the milliwatt readings versus the cyanide ion concentration on semilog paper. The cyanide concentration is plotted on the log scale and for convenience units of µg CN/25 ml are often used. Standards should be analyzed alternatively with the samples to minimize variation in the readings. Concentrations may be read directly from the calibration curve in units of µg CN/25 ml.

5. RECOVERY CHECK

5.1 It is recommended that the per cent recovery from the filters be checked. This is done by spiking blank filters, in a least duplicate, with a weighable amount of cyanide corresponding to a concentration in the range of interest. Extract and analyze as above, including a blank. If the recovery is less than 94 per cent, the calculated cyanide concentrations should be corrected as follows:

$$\text{Recovery} = \frac{\text{average µg CN recovered}}{\text{µg CN added}}$$

$$\text{Correct µg/sample} = \frac{\text{observed µg/sample}}{\text{recovery}}$$

METHOD 47

(SULPHURIC ACID)

Method No: 47 (NIOSH S174)
Range: 0.561 to 2.577 mg/m^3
Precision: ($\overline{CV}_T$) 0.082
Procedure: Filter collection, titration with barium perchlorate

1. APPARATUS

1.1 The unit for the collection of personal air samples for the determination of organic aerosol has the following components.

1.1.1 The filter unit consisting of the filter media and a polystyrene 37 mm 3-piece cassette filter holder.

1.1.2 Personal Sampling Pump

1.1.3 Thermometer

1.1.4 Manometer

1.1.5 Stopwatch

1.2 Mixed cellulose ester membrane filter, 0.8 micrometre pore size and 37 mm diameter. The filter is held in the three piece cassette supported by a cellulose backup pad.

1.3 Screw cap bottles. Within 1 hour after the sample has been collected, the filter is transferred to a clean screw cap bottle (a 45 mm tissue sample holder is satisfactory) for shipping.

1.4 Erlenmeyer flasks, 125 ml.

1.5 Pipets, 2 ml or convenient sizes.

1.6 Burette. A burette of 10 ml capacity graduated in 0.05 ml.

1.7 Daylight fluorescent lamp aids in identifying the end point.

1.8 Ion Exchange Resin. Dowex 50W-X8, 20/50 mesh, hydrogen form ion exchange columns may be constructed using glass burettes or tubing. A column with an inside diameter of 8 mm and 7 inches of resin has a capacity of approximately 25 milli-equivalents. This is used to purify the standard sulfate solution and for samples which might contain possible interferring metal ions. When about two-thirds of the resin's capacity has been exhausted, (deterioration in sharpness of the endpoint), regenerate the resin by passing 30 ml of 4 M hydrochloric acid through column.

After charging and thorough washing with distilled water, the column is ready for use.

1.9 Volumetric flasks, 1 litre, or convenient sizes for preparation of standard solutions.

2. REAGENTS

2.1 Double distilled water.

2.2 Isopropanol, reagent grade.

2.3 Anhydrous sodium sulfate, reagent grade. Prepare a 0.005 M sodium sulfate solution. Pass this solution slowly through the ion exchange resin and collect the solution in a clean 1 litre volumetric flask.

2.4 Barium Perchlorate, 0.005 M. Dissolve 2.0 g of barium perchlorate trihydrate in a 1 litre volumetric flask with distilled water and make up to volume. Standardize the solution against the sodium sulfate standard. Into a 125 ml erlenmeyer flask, pipet 5 ml of the sodium sulfate standard and 40 ml of isopropanol. Adjust the pH to 3.5 with perchloric acid. Add 3 drops of Thorin, and titrate against barium perchlorate to the end point.

2.5 Hydrochloric Acid, 4M. Add 300 ml concentrated hydrochloric acid to 600 ml distilled water. The hydrochloric acid is used to regenerate the ion exchange column.

2.6 Perchloric Acid, 1.8%. Dilute 25 ml of reagent grade perchloric acid (70-72%) to 1 litre with distilled water.

2.7 Thorin. Prepare a 0.1%-0.2% solution in distilled water.

2.8 Concentrated nitric acid

2.9 Concentrated sulfuric acid

2.10 pH paper, Hydrion

METHOD 47

(SULPHURIC ACID)

(cont'd)

3. PROCEDURE

3.1 Cleaning of Equipment. All glassware used for the laboratory analysis, as well as the screw cap bottles, should be detergent washed and thoroughly rinsed with tap water and distilled water, followed by acid washing in concentrated nitric acid. Rinse with distilled water.

3.2 Calibration of Personal Sampling Pumps. See Method No. 1a.

3.3 Collection of Samples:

3.3.1 Assemble the filter in the three-piece filter cassette holder and close firmly to ensure that the centre ring seals the edge of the filter. The cellulose membrane filter is held in place by a cellulose backup pad.

3.3.2 Remove the cassette plugs and attach to the personal sampling pump tubing. Clip the cassette to the worker's lapel.

3.3.3 A sample size of 180 litres is recommended. Sample at a flow rate of 1.5 litres per minute. The flow rate should be known with an accuracy of $\pm$ 5%.

3.4 Analysis of Samples:

3.4.1 Open the screw cap bottle containing the filter, and pipet 2 ml of distilled water into the bottle. Let it stand for 5 to 10 minutes.

3.4.2 Transfer the rinse to a 125 ml erlenmeyer flask.

3.4.3 Add 3 ml isopropyl alcohol to the screw cap bottle, and let it stand for 5 to 10 minutes.

3.4.4 Transfer the isopropyl alcohol-rinse to the erlenmeyer flask. Repeat steps 3.4.3 and 3.4.4 once more.

3.4.5 Add an additional 10 ml isopropyl alcohol to the erlenmeyer flask.

3.4.6 Adjust the pH of the solution in the flask with 1.8% perchloric acid to a value between 2.5-4.0. One or two large drops of the perchloric acid should be enough to adjust the pH.

3.4.7 Add 3 drops of Thorin to the erlenmeyer flask.

3.4.8 Titrate the sample with 0.005M barium perchlorate to an apricot-coloured end point.

4. CALIBRATION AND STANDARDS

The barium perchlorate solution is standardized by titrating the ion exchanged sodium sulfate standard to the end point with Thorin as the indicator. (See Section 2.4). The molarity of $Ba(ClO_4)_2$ is calculated as follows:

$$M_{Ba(ClO_4)_2} = \frac{ml_{Na_2SO_4} \times M_{Na_2SO_4}}{ml_{Ba(ClO_4)_2}}$$

where:

$ml_{Na_2SO_4}$ = ml Na_2SO_4 solution needed to titrate $Ba(ClO_4)_2$

$M_{Na_2SO_4}$ = Molarity of Na_2SO_4

$ml_{Ba(ClO_4)_2}$ = ml $Ba(ClO_4)_2$ used

The molarity of $Ba(ClO_4)_2$ should be checked periodically.

5. CALCULATIONS

5.1 The following reaction is the basis for this analytical method:

$$H_2SO_4 + Ba(ClO_4)_2 \rightarrow BaSO_4 \downarrow + 2HClO_4$$

5.2 The mg of $H_2SO_4 = M_{Ba(ClO_4)_2} \times ml_{Ba(ClO_4)_2} \times 98$

where:

$M_{Ba(ClO_4)_2}$ = Molarity of $Ba(ClO_4)_2$ solution

$ml_{Ba(ClO_4)_2}$ = ml of $Ba(ClO_4)_2$ solution needed to titrate the sample

98 = Molecular weight of H_2SO_4

5.3 Corrections for the blank must be made for each sample if an end point can be seen from the blank filter.

$$mg = mg\ sample - mg\ blank$$

where:

mg sample = mg found in sample filter

mg blank = mg found in the blank filter

5.4 The concentration of H_2SO_4 can be expressed in mg/m^3.

$$mg/m^3 = \frac{mg \times 1000\ litre/m^3}{Air\ Volume\ Sampled\ (litre)}$$

6. REFERENCES

1. Fritz, J.S., and Yamamura, S.S., Anal. Chem., 27 1461 (1955).

2. Leithe, W., "The Analysis of Air Pollutants", An Arbor Science Press, 1970.

3. Kundig, Chem. Rundechau, 18, (1965).

4. Fielder and Morgan, Anal. Chem Acta, 23, 538 (1960).

5. Fielder and Morgan, Z. Anal. Chem., 183, 455 (1961).

6. Documentation of NIOSH Validation, NIOSH Contract No. CDC-99-74-45.

METHOD 48a

(TETRAETHYL LEAD AND TETRAMETHYL LEAD)

Method No: 48a(NIOSH S383)
Range: 0.045 to .020 mg/m^3 (as Pb)
Precision: ($\overline{CV}_T$) 0.087
Procedure: Adsorption on XAD-2, desorption with pentane, GC/photo-ionization detection.

1. APPARATUS

1.1 Sampling Apparatus

1.1.1 A calibrated personal sampling pump.

1.1.2 Resin tubes. Glass tube with both ends flame-sealed, 10 cm long with 6 mm O.D. and 4 mm I.D., containing 2 sections of 20/50 mesh XAD-2 resin. The adsorbing section contains 100 mg of resin, the backup section 50 mg. A small wad of silylated glass wool is placed between the front adsorbing section and the backup section; a plug of silylated glass wool is also placed in front of the adsorbing section and at the end of the backup section.

1.1.3 Barometer

1.1.4 Thermometer

1.1.5 Stopwatch

1.2 Gas chromatograph. The unit must be equipped with a photo-ionization detector.

1.3 Column. (10 ft. x 1/8 in. I.D. stainless steel) packed with 5% Carbowax 20M stationary phase on 80/100 mesh Chromosorb WAW.

1.4 An electronic integrator or some other suitable method for measuring peak areas.

1.5 Two millilitre sample containers with glass stoppers or Teflon lined caps. If an automatic injector is used, the associated vials are acceptable.

1.6 Microlitre syringes. 10, 20, 50, 100 and 250 microlitre and other convenient sizes for preparing standards.

1.7 Pipet. 1 ml delivery type.

1.8 Volumetric flasks. 10 ml or convenient sizes for making standard solutions and internal standard solutions.

METHOD 48a

(TETRAETHYL LEAD AND TETRAMETHYL LEAD)

(cont'd)

2. REAGENTS

2.1 Pentane, reagent grade.

2.2 Tetraethyl lead

2.3 Dodecane or other suitable internal standard. The appropriate solution of the internal standard is prepared in pentane.

2.4 Nitrogen, purified

2.5 Pre-cleaned resin: XAD-2 resin (20-50 mesh) can be obtained from the Rohm and Haas Company. XAD-2 resin is purified by charging an amount into a Soxhlet extractor. Larger batches may be prepared by using a Giant extractor. Overnight (24 hours) extractions are then performed successively with water, methanol, diethylether and finally, n-pentane. Distilled-in-glass solvents are used in all cases. Resin has been prepared in this manner using charges of about 700g of resin and 1.5 litres of each solvent. The resin is dried by maintaining it under vacuum (1-10 torr) and mild heat for about 24 hours.

3. PROCEDURE

3.1 Cleaning of equipment. See Method No. 1a.

3.2 Calibration of Personal Pumps. See Method No. 1a.

3.3 Collection of Samples:

3.3.1 A sample size of 120 litres is recommended. Sample at a flow rate of 1.0 litre per minute for 120 minutes. The flow rate should be known with an accuracy of at least $\pm$ 5%.

3.4 Analysis of Samples:

3.4.1 Preparation of Samples. See Method No. 1a.

3.4.2 Desorption of Sample. Prior to analysis, 1.0 ml of pentane is pipetted into each sample container. Desorption should be done for 30 minutes.

3.4.3 GC Conditions. The typical operating conditions for the gas chromatograph are:

1. 20 ml/min (60 psig) nitrogen carrier gas flow
2. 185°C injector temperature
3. 200°C manifold temperature
4. 210°C photoionization detector temperature
5. 75°C column temperature

3.4.4 A 5 microlitre aliquot of the sample solution is injected into the gas chromatograph.

4. CALCULATIONS

4.1 Read the weight, in µg of lead, corresponding to each peak area from the standard curve. No volume corrections are needed, if the standard curve is based on µg per 1.0 ml pentane and the volume of sample injected is identical to the volume of the standards injected.

5. REFERENCES

1. Memoranda, Kenneth A. Busch, Chief, Statistical Services, DLCD, to Deputy Director, DLCD, dated 1/16/75, 11/8/74, subject: "Statistical Protocol for Analysis of Data from Contract CDC-99-74-45".

2. Backup Data Report for Tetraethyl lead, No. S383, prepared under NIOSH Contract No. 210-76-0123.

3. Final Report, NIOSH Contract HSM-99-71-31, "Personal Sampler Pump for Charcoal Tubes", September 15, 1972.

METHOD 48b

(TETRAMETHYL LEAD AND TETRAETHYL LEAD)

Method No: 48b
Range: Unknown
Precision: Unknown
Procedure: Collection on glass-fibre iodized carbon filter, colorimetric.

1. APPARATUS

1.1 Personal Sampling Pump.

1.2 Pitman lead-in-air analyses, Model 705 or equivalent.

2. REAGENTS

2.1 The following ampouled reagents (D.A. Pitman Ltd.) are supplied for use with the lead-in-air analyses.

2.2 Iodine, 0.2N in methanol.

2.3 Iodine, 2N aqueous solution in KI.

2.4 Solution A. A lead-free aqueous solution of potassium cyanide, sodium sulphite, ammonium citrate and ammonium hydroxide contained in two ampoules. (Reference 2).

2.5 Dithizone in chloroform, 40 mg/l.

3. COLLECTION OF SAMPLES

3.1 Preparation. See Method No. 48c.

3.2 Sampling. See Method No. 48c.

4. ANALYSIS OF SAMPLES

4.1 After sampling, dismantle the filter holder and transfer the carbon filter into a midget impinger tube.

4.2 Add 15 ml of 0.2N iodine in methanol, stopper the tube and shake the contents for 1 min.

4.3 Add 10 ml of 2.0 N iodine in aqueous potassium iodide solution and swirl the tube to mix the solution.

4.4 Warm the solution to at least 27°C and hold it at this temperature for a minimum of 5 min.

4.5 Filter the iodine solution through a glass-wool plug into a flask.

4.6 Add 35 ml of solution A to the flask.

4.7 Stopper the flask and shake until the iodine is completely decolorised.

4.8 Pour 5 ml of chloroform into the vial containing 0.2 mg of dry dithizone and add this solution to the flask.

4.9 Shake the flask vigorously for 30 sec. and allow the two layers of liquid to separate.

4.10 If a red layer is obtained in the lower layer and the upper layer is orange-yellow, place the flask in the Lovibond Comparator and rotate colour disc until a colour match is obtained.

Notes:

1. If an orange or red-orange colour is obtained in the chloroform layer, an incomplete reaction of organic lead with the iodine is indicated. The analysis must be repeated, making sure that the solution is heated to and held at a minimum temperature of 27°C for at least 5 minutes to permit complete reaction of the lead compounds with the iodine.

2. If the upper layer does not appear yellow and the colour of the chloroform layer is darker than the deepest shade on the disc, insufficient dithizone is present and another portion of dithizone should be added. Shake the comparator flask for a further 30 seconds and obtain a colour match. If the colour is still too deep for matching, then it will be necessary to repeat the test but running for a shorter length of time.

4.11 Carry out a blank determination using a treated glass-fibre-carbon filter.

5. REEFERENCES

1. S.E. Birnie and F.G. Noden, Analyst. 105 110 (1980).

2. L.J. Snyder and S.R. Henderson, Anal. Chem. 33, 1175 (1961).

METHOD 48c

(TETRAMETHYL LEAD AND TETRAETHYL LEAD)

Method No: 48c
Range: Unknown
Precision: Unknown
Procedure: Collection on glass-fibre iodized carbon filter, extraction with nitric acid-bromine reagent, AAS with electrothermal atomization.

1. APPARATUS

1.1 Personal Sampling Pump

1.2 Perkin Elmer 300S Atomic Absorption Spectrophotometer with an HGA-76 carbon furnace atomizer accessory or equivalent.

2. REAGENTS

2.1 25% w/v potassium iodide solution. Dissolve 500 g of potassium iodide in about 1 litre of distilled water. Solution is made alkaline by the dropwise addition of ammonia solution and then de-leaded by shaking with successive 50 ml portions of 20 mg/l of dithizone in chloroform solution until green colour remains unchanged. Separate the organic phase and make the solution slightly acidic by dropwise addition of dilute nitric acid and then wash with $CHCl_3$. Separate $CHCl_3$ layer and make up the volume of the remaining solution to 2 litres with distilled water.

2.2 Iodine monochloride stock solution, 1.0 M. Mix 445 ml of de-leaded 25% w/v potassium iodide solution with 445 ml of concentrated hydrochloric acid. Slowly, with cooling, add 75 g of analytical reagent grade potassium iodate stirring the solution until all of the free iodine has re-dissolved to give a clear orange-red solution; dilute the solution to 1 litre with distilled water.

2.3 50% v/v Nitric acid solution.

2.4 1% v/v Nitric acid solution.

2.5 Bromine, Aristar grade.

2.6 Standard inorganic lead solution, 100 µg/ml. Dissolve 0.160 g of analytical-reagent grade lead nitrate in distilled water, add 10 ml of Aristar-grade concentrated nitric acid and make up the volume to 1 litre with distilled water.

2.7 Standard inorganic lead solution, 0.2 µg/ml.

3. COLLECTION OF SAMPLES

3.1 Preparation: Soak 25 mm diameter Whatman glass fibre - carbon filters, grade ACG/B, in 0.2 N methanolic iodine for 15 min. Remove the filters using ivory-tipped forceps and allow them to dry in a dessicator for 2 hours.

3.2 Dismantle a Gelman 25 mm diamter, in-line filter holder and, using ivory-tipped forceps, place one of the treated carbon filters centrally on the mesh support.

3.3 Reassemble the holder and using the minimum length of plastic tubing, connect the holder to the pump. Sample for the required period.

4. ANALYSIS OF SAMPLES

4.1 After sampling, dismantle the filter holder and transfer the carbon filter into a 150 ml beaker.

4.2 Add 10 ml of 50% v/v nitric acid and 1 ml of bromine.

4.3 Cover beaker with a watch-glass and warm the solution gently until all of the bromine has evaporated.

4.4 Digest the solution on a hot plate for 1 hour then evaporate the solution almost to dryness.

4.5 Cool, add 10 ml of 1% v/v nitric acid to the residue and warm.

4.6 Filter the solution through a Whatman No. 54 paper to remove any insoluble matter and dilute to 100 ml with 1% v/v nitric acid.

4.7 Inject 20 µl of the solution into the carbon furnace using the following conditions: drying, 10 s at 150°C, ashing, 10 s at 490°C, atomisation, 4 s at 2100°C.

4.8 Carry out a blank determination using a treated glass-fibre-carbon filter.

5. CALIBRATION AND STANDARDS

5.1 Prepare a calibration graph using 0.2 µg/ml standard

inorganic lead solution. The linear range of the calibration is 0 to 2 ng of lead injected.

5.2 Read of the concentration of lead in the sample from the analytical curve.

6. REFERENCE

1. S.E. Birnie, F.G. Noden, Analyst, 105 110 (1980).

METHOD 49

(TITANIUM DIOXIDE)

Method No: 49 (NIOSH S38S)
Range: 8.1 to 29.5 mg/m^3
Precision: ($\overline{CV}_T$) 0.112
Procedure: Filter collection, Acid digestion, Atomic absorption.

1. APPARATUS

1.1 Sampling Equipment - The sampling unit for the collection of personal air samples for the determination of metal content has the following components:

1.1.1 The filter unit, consisting of the filter media and 37 mm, 3-piece cassette filter holder.

1.1.2 Personal Sampling Pump.

1.1.3 Thermometer

1.1.4 Manometer

1.1.5 Stopwatch

1.2 Mixed cellulose ester membrane filter; 37 mm diameter, 0.8 micrometer pore size.

1.3 Atomic absorption spectrophotometer, having a monochromator with a reciprocal linear dispersion of about 6.5 Angstrom/mm in the ultraviolet region. The instrument must have the burner head for a nitrous oxide-acetylene flame.

1.3.1 Titanium hollow cathode lamp.

1.3.2 Nitrous oxide

1.3.3 Fuel: purified acetylene

1.3.4 Pressure regulators, two-stage, for each compressed gas tank used.

1.4 Glassware, borosilicate: Use glassware only if fluorides are absent.

1.4.1 125 ml Phillips beakers with watchglass covers.

1.4.2 Pipets, delivery or graduated, 1, 5, 10 ml and other convenient sizes for making standards.

1.4.3 50 ml volumetric flasks.

1.5 Adjustable thermostatically-controlled hot plate capable of reaching 400°C.

2. REAGENTS

All reagents used must be ACS Reagent Grade or better.

2.1 Distilled or deionized water

2.2 Concentrated nitric acid

2.3 Nitric acid, 0.1N

2.4 Concentrated sulfuric acid

2.5 Sulfuric acid/ammonium sulfate mixture. Dissolve 40 g of ammonium sulfate in 100 ml of sulfuric acid.

2.6 Aqueous standard titanium stock solution, 500 µg/ml as titanium. Dissolve 0.4170 g of dried, analytical reagent grade titanium dioxide in 25 ml of the sulfuric acid/ammonium sulfate mixture. Dilute to 500 ml with water in a volumetric flask. A commercially available titanium stock solution (1000 µg/ml) may also be used.

3. PROCEDURE

3.1 Cleaning of Equipment:

3.1.1 Before use, all glassware should initially be soaked in a mild detergent solution to remove any residual grease or chemicals.

3.1.2 After initial cleaning, the glassware should be thoroughly rinsed with warm tap water, concentrated nitric acid, tap water, and distilled water, in that order, and then dried.

3.2 Collection of Samples:

3.2.1 To collect titanium dioxide dust, a personal sampler pump is used to pull air through a cellulose ester membrane filter.

3.3 Analysis of Samples:

3.3.1 Open the cassette filter holder and carefully remove the cellulose membrane filter from the holder and cellulose backup pad with the aid of Millipore filter tweezers and transfer filter to a 125 ml Phillips beaker. Rinse the inner portion of the cassette holder with distilled water and transfer rinsings to Phillips beaker.

3.3.2 Wet ashing. To destroy the organic filter matrix, treat the sample in each beaker with 3 ml of concentrated nitric acid. Cover each beaker with a watch glass and heat on a hot plate (140^{o}) in a fume hood until all the filter is dissolved and the volume is reduced to about one-half millilitre. Repeat this process once more using 3 ml of concentrated nitric acid. Do not allow the solution to evaporate to dryness. Cool solution.

3.3.3 Titanium dioxide dissolution. To ensure complete dissolution of titanium dioxide, add 8 ml of the sulfuric acid/ammonium sulfate mixture and continue heating on a high temperature hot place (400^{o}) until all the remaining solids completely dissolve. This heating cycle will require the dissolution process, add a couple of glass beads. Do not allow the solution to evaporate to dryness at any point. If fluorides are present, some loss of titanium due to formation of titanium tetrafluoride may occur.

3.3.4 Cool solutions and add 10 ml of distilled (or deionized) water to each one.

3.3.5 Quantitatively transfer the clear solutions into a 50 ml volumetric flask.

3.3.6 Rinse each beaker at least twice with 5 ml portions of distilled water, and quantitatively transfer each rinsing to the solution in the volumetric flask. Dilute to volume.

NOTE: If fluorides are known to be present, add 5 ml of IN ammonium fluoride before diluting to volume.

3.3.7 Aspirate the solutions into a reducing nitrous oxide-acetylene flame and record the absorbance at 364.3 nm. The absorbance is proportional to the sample concentration and can be determined from the appropriate calibration curve.

3.3.8 Appropriate filter blanks must be analyzed by the same procedure used for the samples.

METHOD 49

(TITANIUM DIOXIDE)

(cont'd)

4. CALIBRATION AND STANDARDS

4.1 From the standard titanium stock solution, prepare at least six working standards to cover the titanium concentration range from 0.2 to 3.0 mg/ml. Add 8 ml of the sulfuric acid/ ammonium sulfate mixture to each of these working standard solutions and dilute to 50 ml with 0.1N nitric acid. Prepare these working standards fresh daily.

4.2 Proceed as in Section 3.3.7.

4.3 Prepare a calibration curve by plotting on linear graph paper the absorbance versus the concentration of each standard in mg/50 ml. It is advisable to run a set of standards both before and after the analysis of a series of samples to ensure that conditions have not changed.

5. CALCULATIONS

5.1 Read the weight, in mg, corresponding to the total absorbance from the standard curve. No volume corrections are needed, if the standard curve is based on mg per 50 ml. Note that the data will be in mg of titanium. Convert to titanium dioxide by multiplying with the molecular weight ratio, 79.89/47.9 = 1.667.

See method No. 1a for computation of results.

6. REFERENCES

1. Analytical Methods for Atmomic Absorption Spectrophotometry, the Perkin-Elmer Corporation, Norwalk, Conn., 1971.

2. Methods for Emission Spectrochemical Analysis, ASTM Committee E-2, Philadelphia, 1971.

3. "Documentation of NIOSH Validation Tests", Contract No. CDC-99-74-45.

4. Bond, A.M. "Use of Ammonium Fluoride in Determination of Zirconium and Other Elements by Atomic Absorption Spectrometry in the Nitrous Oxide-Acetylene Flame", Anal. Chem. 42, 932 (1970).

METHOD 50

(2,4-TOLUENE DIISOCYANATE (TDI))

Method No: 50 (AMP-110)
Range: Unknown
Precision: Unknown
Procedure: Collection on "Tenax sampling tubes, desorption with n-hexane, G.C.

1. APPARATUS

1.1 Gas chromatograph (GC) equipped with a flame ionization detector and an appropriate recorder.

1.2 Column, 2 m in length and of 2 mm inside diameter (I.D.), stainless steel, packed with 3% "OV-17" on "Chromosorb G", 80-120 mesh, conditioned for approximately 12 hours at 190°C, with a nitrogen gas flow rate of 20 ml/min.

1.3 Sampling tubes, 15 cm by 1.3 cm, glass, packed with "Tenax" 30-60 mesh, pre-purified and conditioned.

1.4 Air sampling pump with "Teflon" diaphragm or equivalent diaphragm which does not absorb or desorb organic vapours.

1.5 Flow metre, to measure sampling flow rate.

1.6 Glass stoppered glass containers suitable for shipping TDI solutions.

1.7 Wrapping paper, non-translucent.

2. REAGENTS

2.1 Hydrogen, ultra-high purity, 99.99% H_2 minimum.

2.2 n-hexane, C.P.

2.3 Clean air, total hydrocarbon content less than 0.1 ppm as methane. The n-hexane content should be less than 0.01 ppm by volume as tested by G.C.

2.4 Nitrogen, ultra-high purity, 99.99% N_2 minimum.

2.5 Toluene-2,4-diisocyanate, $CH_3C_6H_3(NCO)_2$, C.P.

2.6 Column packing material "OV-17".

2.7 Column packing material "Chromosorb G", 80-120 mesh.

METHOD 50

(2,4-TOLUENE DIISOCYANATE (TDI))

(cont'd)

2.8 Acetone, C.P.

2.9 "Tenax" adsorbent, 30-60 mesh.

2.10 Anisaldehyde, $C_8H_8O_2$, C.P.

3. PROCEDURE

3.1 "Tenax" used for the adsorption of TDI in the sampling tubes is purified by thoroughly rinsing first with acetone, then with n-hexane, and finally by conditioning at a temperature of 140-150°C for about 12-15 hours. A sampling tube containing the purified "Tenax" is treated with n-hexane at room temperature, and the resulting extract is tested by GC for the presence of interfering compounds.

3.2 Sampling:

3.2.1 The air to be sampled is passed at pre-determined rates and volumes through "Tenax" sampling tubes and any adsorbed TDI is chemically desorbed from the resin at room temperature, by immediately pouring 10 ml of n-hexane through the vertically positioned sampling tubes. The resulting solutions of TDI are shipped in glass stoppered glass containers protected from light and heat to the laboratory. Analysis should be carried out within a 12-hour period after collection of the samples.

3.3 Gas chromatographic procedure.

3.3.1 The chromatograph, equipped with a flame ionization detector and a column packed with 3% "OV-17" on "Chromosorb G", is set to the following conditions:

1. Column temperature: 120°C (isothermal)
2. Detector temperature: 250°C
3. Injector temperature: 175°C
4. Nitrogen carrier gas flow rate: 55 ml/min.
5. Hydrogen gas flow rate: 30 ml/min.
6. Clean Air flow rate: 300 ml/min.
7. Sample size injected: 5 µl

Before any gas chromatographic analyses are carried out, the gas chromatographic column is conditioned with repeated injections (about 20 times) of 10 µl volumes of a TDI solution made up by dissolving 5 mg TDI in n-hexane to a total volume of 10 ml.

The retention time for TDI under these gas chromatographic conditions is 10.8 minutes.

3.4 Sample Analysis:

3.4.1 Samples are analysed as described in 4.1, with the sample substituting for the calibration standard.

4. CALIBRATION STANDARDS

4.1 Standards of TDI for gas chromatographic analysis are prepared daily by making up solutions of TDI in n-hexane at suitable concentration levels, e.g. 2,4,8,12 and 16 ppm (wt/vol.). By measuring the corresponding peak heights on the gas chromatographic scans of these standard TDI solutions, the response factors, (Peak Height/TDI weight), are calculated for each concentration level. The average response factor value (R.F.) obtained from these standard solutions is the factor used for quantitating TDI in a sample, see 5.1.

4.2 External standard:

4.2.1 Anisaldehyde is a stable external standard used for recognizing changes in detector response. Such changes may either be caused by the instability of TDI in calibration standards or by loss of sensitivity of the detector itself.

This external standard also indicates consistency of retention times of TDI and other compounds eluting from the gas chromatographic column.

A solution of 1 µl anisaldehyde in 50 ml of n-hexane is prepared to obtain a 20 ppm external standard. Other suitable concentrations of this standard are prepared as required. Retention time for anisaldehyde under the gas chromatographic conditions shown is 10.0 minutes.

5. CALCULATIONS

5.1 The concentration of TDI in air is calculated from its chromatographic peak as follows:

$$C = (P)(VH)(RF)(VI)(VA)$$

Where:

C = Concentration of TDI in air, (ng/m^3).
P = Peak height (mm)
RF = Response factor (ratio of peak height of the standard in mm to the weight of TDI in ng).
VH = Volume of n-hexane extrace, (μl).
VI = Volume of injected extract, (μl).
VA = Volume of air, (m^3).

METHOD 51

(VANADIUM, V_2O_5 FUME)

Method No: 51 (S388)
Range: 0.060 - 0.29 mg/m^3
Precision: CV_T 0.067
Procedure: Filter collection, alkali dissolution, flameless AAS/HGA

1. APPARATUS

1.1 Sampling Equipment. The sampling unit for the collection of personal air samples for the determination of metal content has the following components:

1.1.1 The filter unit, consisting of the filter media section 1.2 and 37-mm 3-piece cassette filter holder.

1.1.2 Personal Sampling Pump: A calibrated personal sampling pump whose flow can be determined to an accuracy of ±5% at the recommended flow rate. The pump must be calibrated with a filter holder and filter in the line.

1.1.3 Thermometer

1.1.4 Barometer

1.1.5 Stopwatch

1.2 Mixed cellulose ester membrane filter: 37-mm diameter, 0.8 micrometer pore size.

1.3 Atomic absorption spectrophotometer, having a monochromator with a reciprocal linear dispersion of about 6.5 Angstrom/mm in the ultraviolet region. The instrument must have a high temperature graphite atomizer (HGA) and a deuterium arc background corrector.

1.3.1 Vanadium hollow cathode lamp.

1.3.2 Deuterium arc lamp.

1.3.3 Purge gases: Argon (for HGA), Nitrogen (for Deuterium arc)

1.3.4 Pressure regulators, two-stage, for each compressed gas tank used.

1.4 Glassware, borosilicate:

1.4.1 50 ml beakers with watchglass covers.

1.4.2 Pipetes, delivery or graduated 1, 5, 10 ml and other convenient sizes for making standards.

1.4.3 10 ml volumetric flasks.

1.5 Water bath maintained at 50°C.

2. REAGENTS

2.1 Water, distilled or deionized.

2.2 Sodium hydroxide, 0.01N

2.3 Standard stock solutions containing 100 µg/ml of vanadium pentoxide. This solution can be prepared by dissolving 0.100 g V_2O_5 in 0.01N sodium hydroxide and diluting to 1.0 litre with 0.01N NaOH.

2.4 V_2O_5 working standard solution, 1.0 µg/ml. Prepare by appropriate dilution of above solution with 0.01N sodium hydroxide. Prepare fresh each day.

3. PROCEDURE

3.1 Cleaning of Equipment:

3.1.1 Before use, all glassware should be initially soaked in a mild detergent solution to remove any residual grease or chemicals.

3.1.2 After initial cleaning, the glassware should be thoroughly rinsed with warm tap water, 6 ml nitric acid, tap water and distilled or deionized water, in that order, and then dried.

3.2 Collection of Samples:

3.2.1 To collect V_2O_5 fume, a personal sampler pump is used to pull air through a cellulose ester membrane filter (Section 1.1). The filter holder is held together with tape or a shrinking band. If the middle piece of the filter holders does not fit snugly into the bottom piece of the filter holder, the contaminant will leak around the filter. A piece of flexible tubing is used to connect the filter holder to the pump. Sample at a flow rate of 1.5 litres per minute for 15 minutes with face cap on and small plugs removed. After sampling, replace small plugs.

3.2.2 Blank. With each batch of ten samples submit one filter from the same lot of filters which was used for sample collection and which is subjected to exactly the same handling as for the samples except that no air is drawn through it. Label this as a blank.

3.3 Analysis of Samples:

3.3.1 Open the cassette filter holder and carefully remove the cellulose membrane filter from the holder and cellulose backup pad with the aid of appropriate tweezers. Transfer filter to a 50 ml beaker.

3.3.2 V_2O_5 dissolution. To ensure complete dissolution of V_2O_5 from the filter, add 5 ml of 0.01N NaOH to the beaker and heat in a water bath at 50°C for 15 minutes.

3.3.3 Cool solutions and quantitatively transfer the clear solutions into a 10 ml volumetric flask.

3.3.4 Rinse each beaker at least twice with 1-2 ml portions of 0.01N NaOH, and quantitatively transfer each rinsing to the solution in the volumetric flask.

3.3.5 Dilute all samples to 10 ml with 0.01N NaOH.

3.3.6 Inject 50 µl of solution into a high temperature graphite atomizer. Dry at 125°C for 40 seconds, char at 500°C for 10 seconds and atomize at 2700°C for 20 seconds. Use the deuterium arc lamp to correct for "smoke" produced by the matrix. Record the absorbance at 318.4 nm. The absorbance is proportional to the sample concentration and can be determined from the appropriate calibration curve if the graphite tube in use gives reproducible results.

3.3.7 Appropriate filter blanks must be analyzed by the same procedure used for the samples.

4. CALIBRATION AND STANDARDS

4.1 From the standard V_2O_5 working standard solution, prepare at least six calibration standards to cover the V_2O_5 concentration range from 0.5 to 7 µg per 10 ml. Prepare these calibration standards fresh daily and make all dilutions with 0.01N NaOH. (Express concentration as µg V_2O_5 per 10 ml.

4.2 Proceed as in Section 3.3.7.

4.3 Prepare a calibration curve by plotting on linear graph paper the absorbance versus the concentration of each standard in µg/10 ml. Special care must be given to proper calibration due to irregular behavior of some graphite tubes.

4.4 In cases where a calibration curve could not be used realiably, determine the appropriate response factor. To determine the response factor, the appropriate calibration standards are alternately analyzed with the samples. This practice will minimize the effect of observed fluctuations or variations in absorbance and peak width readings during any given day.

5. CALCULATIONS

5.1 Read the weight, in µg, corresponding to the total absorbance from the standard curve. No volume corrections are needed, if the standard curve is based on µg per 10 ml. Or alternatively, determine the weight in micrograms corresponding to the absorbance area of the sample by using the appropriate response factor determined from the response of the calibration standard. All data are expressed as V_2O_5.

5.2 See method No. 1a.

6. REFERENCES

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METHOD 52

(VINYL ACETATE)

Method No: 52 (P & CAM 278)
Range: 8 to 210 mg/m^3 in 1.5 litres of air
Procedure: Adsorption on Chromosorb 107, thermal desorption, GC-FID

1. APPARATUS

1.1 Personal sampling pump.

1.2 Chromosorb 107 sampling tubes. Individual front and backup tubes (Century Systems Corporation "Flare" tubes or equivalent) are used.

1.3 Thermal desorber equipped with thermostatted desorbing oven, 300 ml sample reservoir, and a 2 ml gas sampling loop (Century Systems Corporation Programmed Thermal Desorber or equivalent).

1.4 Gas chromatograph equipped with a flame ionization detector and electronic integrator.

1.5 GC column (20 ft. x 1/8 in. O.D.) made of silanized stainless steel and packed with 10% FFAP on 80/100 mesh Chromosorb WAW.

1.6 Vials 1.5 ml, with aluminum serum cups equipped with Teflon lined silicone rubber septa.

1.7 Microlitre syringes, 10 µl, and convenient sizes for making standards.

1.8 Macropipette, 1000 µl, with disposable plastic tips.

1.9 U-tube, glass with at least one hose connection, approximately 75 ml internal volume.

1.10 Pump capable of drawing 200 ml/min through a front section of the sampling device.

1.11 Gas bag, 10 litre volume for helium purge gas.

1.12 Test tubes with close fitting plastic caps.

1.13 Ring stand with clamps.

2. REAGENTS

Whenever possible, reagents used should be ACS Reagent Grade or better.

2.1 Vinyl acetate, practical, inhibited with hydroquinone and freshly distilled before use.

2.2 Hexane, (UV grade)

2.3 Helium, Bureau of Mines Grade A.

2.4 Hydrogen, prepurified

2.5 Filtered, compressed air.

3. PROCEDURE

3.1 Cleaning of Equipment. See Method No. 1a.

3.2 Collection of Samples:

3.2.1 The volume sampled should not exceed 3 litres sampled at a flow rate of 0.1 l/min or less. See Method No. 1a.

3.3 Analysis of Samples:

3.3.1 Preparation of Samples. Remove the caps from either a front or a back section. Wipe the outside of the tube with a clean laboratory wiper.

3.3.2 Thermal Desorber Conditions. Typical operating conditions for the thermal desorber are:

1.	Desorbing oven temperature	150°C
2.	Desorbing rate, helium gas	70 ml/min
3.	Transfer line temperature	160°C
4.	Pressure equalization time	15 sec.

3.3.3 Gas Chromatographic Conditions. Typical operating conditions for the gas chromatograph are:

1.	Helium carrier gas flow rate	33 ml/min
2.	Hydrogen flow to detector	40 ml/min
3.	Air flow to detector	435 ml/min
4.	Injector temperature	160°C
5.	Manifold (detector) temperature	160°C
6.	Oven temperature	60°C

3.3.4 Thermal Desorption of Samples. Wipe off the tube and insert it in the desorbing oven. Desorb with helium at atmospheric pressure. The helium is stored in the 10 litre gas bag. Desorbing with air chars the Chromasorb and renders it unsuitable for reuse.

3.3.5 Injection: Inject a 2 ml aliquot of the desorbed vapours into the GC column.

4. CALIBRATION AND STANDARDIZATION

4.1 It is convenient to express the concentration in terms of µg of vinyl acetate per sample tube. Standard curves are prepared by loading clean sampling tubes (front sections) with known amounts of vinyl acetate. The density of vinyl acetate (0.932 mg/µl at 20°C) is used to convert the volume taken to mass.

4.2 Preparation of Standards. Pipet 1.00 ml aliquots of hexane into clean glass vials. Crimp the vials shut with an aluminum serum cap equipped with a Teflon lined silicone rubber septum. Inject either 25, 10, 5 or 1 µl of freshly distilled vinyl acetate into each vial. These standard solutions are freshly prepared for each analysis.

4.3 Loading the Standard. Support a U-tube on a ring stand. Using a short length of tubing, attach the outlet end of a clean front section of sampling tube to a small pump. The inlet end of the clean front section is attached to the side of the U-tube that has the hose connection. Use the solvent flush technique to withdraw a 2 µl aliquot of a standard solution. Turn on the pump and inject this 2 µl aliquot into the end of the micro tube farthest from the sampling tube. Sweep enough air through the U-tube (2 min at 200 ml/min approximately 5 volume changes) to ensure that all the vinyl acetate is loaded on the sample tube. Stop the pump, remove the sample tube, cap both ends, and label. This tube now contains a known amount of vinyl acetate.

4.4 Standardization. Analyze each tube from Section 4.3 as per Section 3.3. The standard curve is obtained by plotting the amount of vinyl acetate loaded on a tube versus the peak area found. If conditions warrant, prepare standards at higher or lower concentrations.

5. CALCULATIONS

5.1 The sample weight in μg is read from the standard curve.

5.2 Make the appropriate blank corrections.

5.3 The concentration, C, of vinyl acetate in the air sampled is expressed in mg/m^3, which is numerically equal to μg/litre.

$$C = \frac{W_F + W_B}{V}$$

where: W_F = amount of vinyl acetate found on front section in μg

W_B = amount of vinyl acetate found on backup section in μg

V = volume of air sampled in litres

5.4 If desired, the results may be expressed in ppm at 25°C (298°K)

$$C(ppm) = C(\mu g/l) \times \frac{24.45}{86.1} \times \frac{760}{P} \times \frac{T + 273}{298}$$

where: P = pressure of air sampled in torr

T = temperature of air sampled in °C

24.45 = molar volume at 25°C and 760 torr in litres/mol

86.1 = molecular weight of vinyl acetate in g/mol

6. REFERENCES

1. D. L. Foerst, Alexander W. Teass and Maria Risholm-Sundman, "A Sampling and Analytical Method for Vinyl Acetate in Air", (manuscript in preparation). Measurements Research Branch, NIOSH, Cincinnati, Ohio 1978.

METHOD 53

(VINYL CHLORIDE IN AIR)

Method Ref:	53 (P & CAM 178)
Range:	0.008 to 5.2 mg/m^3 in a 5 litre air sample
Precision:	($\overline{CV}_T$) 0.08 at levels of 7 and 71 mg/m^3
Procedure:	Adsorption on activated carbon, desorption with carbon disulfide, gas chromatography

1. APPARATUS

1.1 Personal Sampling Pump. See Method 1a.

1.2 Sorbent Tubes. See Method 1a.

1.3 Gas chromatograph equipped with flame ionization detector.

1.4 Stainless steel column (20 ft x 0.125 in. I.D.) packed with 10% SE-30 on 80/100 mesh Chromosorb W (acid washed, silanized with dimethyl dichlorosilane. Other columns capable of performing the required separations may be used.

1.5 A mechanical or electronic integrator or a recorder and some method for determining peak area.

1.6 Vials (2 ml) that can be sealed with caps containing Teflon-lined silicone rubber septa.

1.7 Microlitre syringes (10 µl, and convenient sizes for making standards).

1.8 Gas-tight syringe (1 ml, with a gas-tight valve).

1.9 Pipettes (0.5 ml delivery pipettes or 1.0 ml type graduated in 0.1 ml increments).

1.10 Volumetric Flasks (10 ml, or convenient sizes for making solutions). It is preferable to have plastic stoppers for the volumetric flasks.

2. REAGENTS

2.1 Carbon disulfide, spectroquality or better grade.

2.2 Vinyl chloride, lecture bottle. 99.9% minimum purity.

2.3 Toluene, chromatographic quality

2.4 Purified helium

2.5 Prepurified hydrogen

2.6 Filtered compressed air

3. PROCEDURE

3.1 Cleaning of Equipment. All glassware used for the laboratory analysis should be washed with detergent and thoroughly rinsed with distilled water.

3.2 Collection of Samples

3.2.1 The flow rate and time, or volume, must be measured as accurately as possible. The smple is taken at a flow rate of 50 ml/min. The maximum volume to be sampled should not exceed 5 litres. See Method 1a.

3.2.2 Relatively large volumes (10 to 20 litres) of air also should be sampled through other sorbent tubes at the same time personal samples are taken. These bulk air samples will be used by the analyst to identify possible interferences before the personal samples are analyzed.

3.3 Analysis of Samples

3.3.1 Preparation and Desorption of Samples. The two tubes used in the collection of a single sample are analyzed separately. Each tube is scored with a file and broken open at each end. The glass wool is discarded. Both sections of each tube are transferred to a small vial containing 1 ml of carbon disulfide. Tests indicate that desorption is complete in 30 min. if the sample is agitated occasionally during this period.

3.3.2 Gas Chromatographic Conditions. The typical operating conditions for the gas chromatograph are:

1. Helium carrier gas flow, 40 ml/min (80 psig)
2. Hydrogen gas flow to detector, 65 ml/min (20 psig)
3. Air flow to detector, 500 ml/min (50 psig)
4. Injector temperature, 230°C
5. Detector temperature, 230°C
6. Column temperature, 60°C

3.3.3 Inject a 5.0 µl aliquot into the GC.

4. CALIBRATION AND STANDARDS

4.1 Standard Preparation:

4.1.1 Gravimetric Method. Vinyl chloride is slowly bubbled into a weighed 10 ml volumetric flask containing approximately 5 ml of toluene. After 3 min, the flask is again weighed. A weight change of 100 to 300 mg is usually observed. The solution is diluted to exactly 10 ml with carbon disulfide and is used to prepare other standards by removal of aliquots with different sized syringes. Subsequent dilution of these aliquots with carbon disulfide results in a series of values that are linear from the range of 0.2 ng per injection, the minimum detectable amount of vinyl chloride, to 1.5 µg per injection.

4.1.2 Volumetric Method. A 1.0 ml gas sample of pure vinyl chloride is drawn into a gas-tight syringe and the valve is closed. The tip of the needle is inserted into a 10 ml volumetric flask containing approximately 5 ml of CS_2. The valve is opened and the plunger is withdrawn slightly to allow the CS_2 to enter the syringe. The action of the vinyl chloride dissolving in the CS_2 creates a vacuum and the syringe becomes filled with the solvent. An air bubble (2%) is present and has been found to be due to the void volume in the needle of the syringe. The solution is returned to the flask and the syringe is rinsed with clean CS_2 and the washings added to the volumetric flask. The volumetric flask is then filled to the mark with CS_2. Other standards are then prepared from this stock solution.

Standards are stored in a freezer at $-20^{\circ}C$ and have been found to be stable at this temperature for three days. Tight-fitting plastic tops on the volumetric flasks seem to retain the vinyl chloride better than ground-glass stoppers.

5. CALCULATIONS

5.1 The weight, in µg, corresponding to the area under each peak is read from the standard curve for vinyl chloride. No liquid volume corrections are needed if the standard curve is based on the number of micrograms in 1.0 ml of CS_2 and the volume of sample injected is identical to the volume of the standards injected. See Method No. 1a for computations of results.

6. REFERENCES

1. Hill, R.H., C.S. McCammon, A.T. Saalwaechter, A.W. Teass, and W.J. Woodfin, "Determination of Vinyl Chloride in Air", in preparation.

2. White, L.D., D.G. Taylor, P.A. Mauer, and R.E. Kupel, "A Convenient Optimized Method for the Analysis of Selected Solvent Vapours in the Industrial Atmosphere". Amer. Ind. Hyg. Ass. J., 31,225 (1970).